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1957

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# solion

PRINCIPLES OF  
ELECTROCHEMISTRY

AND LOW-POWER  
ELECTROCHEMICAL  
DEVICES

FC  
BAC



NAVAL ORDNANCE LABORATORY

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## THE SOLION. PRODUCT OF A NEW ELECTRONIC TECHNOLOGY

### INTRODUCTION

During the past ten years a new technology has been developed at the Naval Ordnance Laboratory, Silver Spring, Md., collaborating more recently under research and development contracts with the Defense Research Laboratory, University of Texas, and the Emhart Manufacturing Company, Hartford, Connecticut.

This technology, chemtronics, involves the movement of ions through a solution, rather than the movement of electrons in space, as in vacuum tubes, or across a solid, as in transistors. The specific electrochemical device developed by this technology is the solion, which is a short designation for "ions in solution". It is pronounced go-lee-on.

Solion transducers have their fundamental basis in the principle of concentration polarization, an effect well known among physical chemists and electroplaters. Physically the solion consists of a plastic cylinder containing a potassium iodide solution in which two or more electrodes are immersed. Polarization is by means of a nine-tenths volt battery. When the unit is stimulated by light, heat, sound, pressure or movement the resultant hydraulic flow within the cell produces a current output. It is reversible.

Although external size is not critical the solions produced to date on a research and development basis by Emhart are of pocket watch size and weight is negligible. These units are characterized by extreme sensitivity and very low power consumption, much less, for example, than that required to operate a comparable transistor system. Other advantages are low cost (once fabrication is put on a mass production basis) small size and weight, simplicity, ease of maintenance and adaptability to mass production.

### APPLICATIONS

A few of the possible fields of application for the solion, at the present state of development, are listed below. Unquestionably the range will be extended as commercial interest in this latest contribution to electronics intensifies and as research and development work is expanded.

1. rate circuits of all descriptions whether operated from temperature, pressure, or electrical, etc., sources,
2. integration units requiring continuous read out of high precision apparently of sufficient accuracy for acceleration guidance systems and small visual exposure meters for personnel protection (similar to film, etc. used for radiation) around jet aircraft engines,
3. detection and measurement of acoustic signals of low frequency (below about 400cps at present) and accelerations, etc.,
4. product circuits involving either electrical derivatives or hydraulic flow or both.
5. electrical and small signal hydraulic amplifiers.
6. computer circuits.
7. amplifiers.

#### HISTORY

The principle of Concentration polarization was explained somewhat empirically by Nernst as early as 1904. By it, the electrical current passing through certain electrochemical systems is limited by diffusion and convection variables such as fluid flow. The principle constitutes one of the basic considerations of the analytical technique known as Polarography, and it comprises one important aspect in the theories of electrochemical over voltage. Quantitative theories, based on mass transfer principles, are prevalent in the chemical and chemical engineering literature, especially since 1946. Much of the early basic quantitative theory has appeared in the literature of England, Russia and certain Russian Satellites.

In 1941, during his employment at the Shell Oil Company, Dr. David Muzzey, now of the Naval Ordnance Laboratory, conceived the idea of using an electrode in solution for acoustic and pressure transducers, such as geophones and accelerometers, etc. He performed such basic studies as were required to show the feasibility of this conception.

During World War II further feasibility studies

(aimed toward ordnance applications) were conducted at NOL by Mr. Elihu Root III and others. In the course of this work it was demonstrated that the iodine-iodide system appeared sufficiently reversible for use in ordnance devices. To date no better universal system has been found. U. S. Patent Number 2,685,025 was issued in 1954 to Mr. Root on some of his work. In 1947, NOL began a concerted effort, under the direction of Mr. N. N. Estes, to apply the results of this early work to specific ordnance devices. A number of basic application problems arose which were not foreseen in the preliminary studies. These were classified in the order of importance and from 1949 on, were studied jointly by NOL and the Defense Research Laboratory of the University of Texas.

Auxiliary studies at NOL showed the then new plastic material Kel-F to be ideally compatible with the iodine-iodide systems. In 1951, NOL and the Emhart Manufacturing Company of Hartford, Conn., began studying techniques for molding this relatively new material into the complex forms required while preserving the rigid purity and exacting dimensional requirements. By 1953 this Company was engaged in manufacturing small quantities of solions for experimental ordnance devices. Emhart is still producing these solions for the Navy.

During this period, the Defense Research Laboratory originated another device complementary to the basic flow detection and integration unit, which, in combination with the flow detector allowed a complete freedom of choice in the design of complex hydraulic-electrical circuits.

The basic theory and technology of solion units is now fairly well understood. It has a large place in the design of hydraulic-electrical circuits complimentary to those of semiconductor devices such as transistors. In many low frequency and integrator applications they are superior devices.

#### PATENT SITUATION

Over the past several years the NOL Patent Staff has processed a large number of employee and contractor invention disclosures relating to Solion devices. Those of importance to the Navy have been filed on in the U. S. Patent Office. Some have issued as patents and can be found in the patented art. Others are still under

prosecution before the U. S. Patent Office or, in some instances, the prosecution has been completed but current military classification prevents their issuance as patents at this time. The Government has retained the entire right, title and interest in all of the inventions with the exception of three which are now patents and in which the Government has a non-exclusive, royalty-free license for governmental use. Persons interested in obtaining a non-exclusive license in any Government owned patent should apply to the Office of Naval Research after the patent has been issued by the U. S. Patent office.

It appears, therefore, that there is an unrestricted field for further application of the solion, variously designed for specific uses, in the commercial field. In closing, of course, there must be inserted a word of caution. A number of technical problems remain to be solved before this class of electrochemical device can be brought into general use as vacuum tubes or transistors are already. Some of these problems can be inferred from the contents of the technical papers included in this brochure. These papers probably constitute the only printed, formal literature presently available on the subject of solions. Further contributions to the art can be anticipated from time to time as interest widens and private research progresses. In this sense the solion follows in the footsteps of the vacuum tube and the transistor along the road to general consumer use. As new industrial applications develop both in the United States and abroad--where interest likewise is mounting--experienced suppliers of the device will increase in number.



PRINCIPLES OF ELECTROCHEMISTRY WHICH ARE BASIC  
TO AN UNDERSTANDING OF ELECTROLYTIC SYSTEMS

by

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Austin, Texas

INTRODUCTION

In recent years an entirely new concept in fluid flow detecting systems has been developed by the Naval Ordnance Laboratory and Defense Research Laboratory. The most outstanding advantage of these new devices over previous ones lies in their very low power consumption, much less, for example, than that required to operate a comparable transistor system.

The component parts of these new systems vary widely in the type of function performed; there are, for instance, fluid flow sensing elements (d.c. and a.c.), units for taking logarithms, derivatives, and products of electrical and/or fluid flow inputs, sensitivity switching elements, etc. All of these individual units, however, may be referred to as electrochemical units, as their operation is based upon fundamental and well-known electrochemical phenomena.

The object of this report is to introduce the reader to those basic principles of electrochemistry directly applicable to the operation of these units, as a knowledge of these principles is essential to the understanding of a second report describing the construction and operation of the units. It is, of course, impossible to give a detailed description of even the most important subjects in electrochemistry in a report of this type. The reader who desires further detail on these subjects is referred to any of several standard textbooks of electrochemistry, preferably one published since 1940.

PART I - FLOW OF ELECTRIC CURRENT THROUGH SOLUTIONS

All conductors of electricity may be divided into two classes, depending upon the type of fundamental particles carrying the current. The first class, metallic conductors, in which the current carriers are exclusively electrons, is familiar to all people in technical work; the second class, electrolytic conductors, is less well-known, as it is studied primarily in the field of elec-

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\*Research on this subject was supported under Bureau Ordnance Contract NOrd-10639 and Contract NOrd-16382

trochemistry. In electrolytic conduction the current carriers are of atomic or molecular size (hence much larger and slower-moving than electrons), and each one may possess either a positive or a negative charge. These carriers are called ions, and are formed by the separation (dissociation) of the components of the molecule of a chemical when it is dissolved in a suitable solvent. An example of an electrolytic conductor is a solution of potassium iodide in water or alcohol; the crystalline salt, when dissolved, dissociates into positively charged potassium ions (written  $K^+$ ) and negatively charged iodide ions ( $I^-$ ). Such a solution is called an electrolytic solution, and the dissolved salt an electrolyte.

If an electric field is imposed across a portion of an electrolytic solution, as for example, by immersion into the solution of two platinum plates connected to the two terminals of a battery, then the positively charged ions (cations) will move toward the plate connected to the negative terminal and the negatively charged ions (anions) toward the opposite plate. Thus the total current carried through the solution is the summation of the individual currents carried by the positive ions moving in one direction and the negative ions moving in the opposite direction. The fraction of the total current carried by the ions of one type is called the transference number of that ion.

The resistance offered by an electrolytic solution to current flow is a function of several things, including the length and area of the electrolytic path, the number and type of ions present, temperature, viscosity of the solvent, etc. In electrochemical work, all the parameters related to the solvent and electrolyte are grouped into a single term called specific conductance,  $L$ , such that:

$$K = \frac{1}{R} = L \frac{A}{\ell}$$

where  $K$  = actual conductance = the reciprocal of solution resistance,  $R$ ;

$A$  = area of electrolytic solution path; and

$\ell$  = length of solution path.

As an example, a column of solution roughly the size of a cigarette, and containing 17 grams of potassium iodide per liter (0.1 Normal) has a resistance of about 750 ohms. Very large changes in resistance may be accomplished by changing the concentration of the electrolyte. For the example just cited, the resistance changes from about 17 megohms for the solvent (water) containing no potassium iodide, down to about 15 ohms for a saturated solution (8 Normal).

## PART II - THE CHANGE FROM METALLIC TO ELECTROLYTIC CONDUCTANCE

A complete electrical circuit containing an electrolytic solution as one of its components is represented diagrammatically in Figure 1. Now since in the metallic portions of the circuit the conduction is exclusively by electrons, while in the electrolytic portion conduction is exclusively by ions, it is

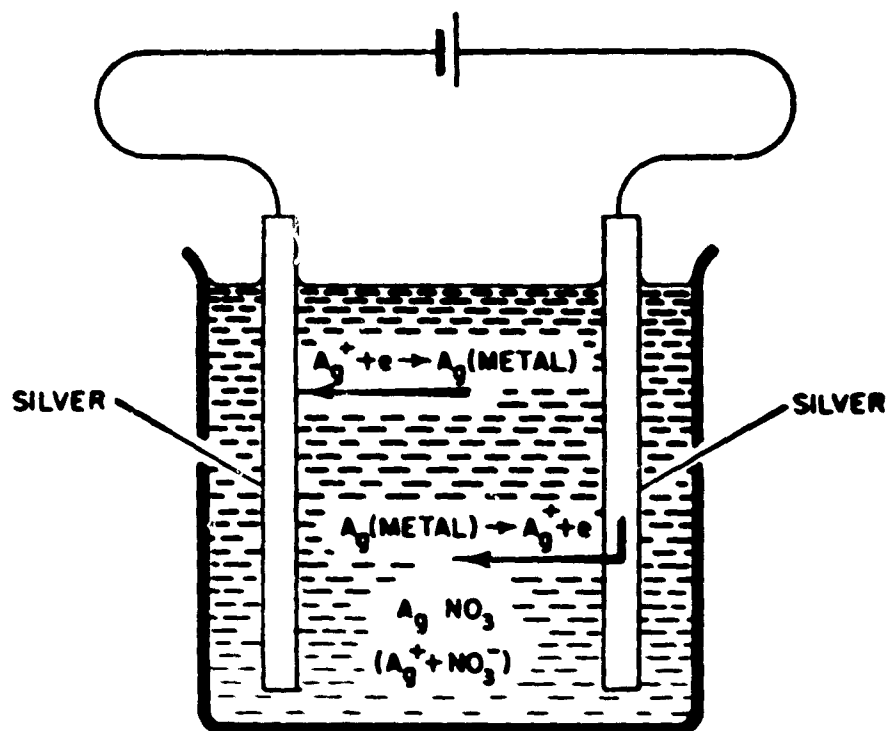


FIG. I - A SIMPLE ELECTRO-CHEMICAL CELL

Obvious that at the metal-electrolyte boundary the type of carrier must change either from electrons to ions or the reverse. This conversion from one type of carrier to the other is accomplished by means of electrochemical reactions, i.e., chemical reactions which involve gain or loss of electrons. A reaction in which the substance reacting loses one or more electrons from its outer electron shell is called an oxidation reaction. Conversely, gain of electrons by the reacting substance is a reduction reaction.

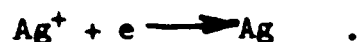
The metallically conducting substances through which the current enters and leaves the solution are known as electrodes; the electrode by which the current enters the electrolyte is known as an anode and the one by which it leaves, as a cathode. As an example, let the electrodes of Fig. 1 be metallic silver (Ag), and the electrolyte a solution of silver nitrate (positive silver ions,  $\text{Ag}^+$ , and negative nitrate ions,  $\text{NO}_3^-$ ). As current flows through the circuit, the following changes occur:

(1) At the anode, metallic silver goes into solution as silver ion, leaving an excess electron in the metal. This reaction, which is the oxidation of silver, is written as:

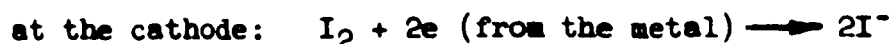


in which  $e^-$  represents the negative electron.

(2) At the cathode, silver ions from the solution acquire an electron from the metal, and are deposited as metallic silver on the cathode. This reaction, the reduction of silver ion, is written:



In the example just cited, the net chemical effect of the passage of current is the dissolution of silver from the anode, with a concurrent deposition of silver on the cathode. It is not necessary, however, for the material of the electrode to enter into the reaction. Thus, platinum plates, immersed in a solution containing iodine ( $\text{I}_2$ ) and potassium iodide (KI), serve only to supply and remove the electrons for the following electrode reactions:



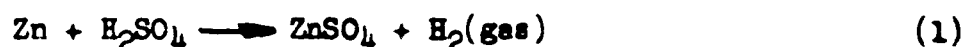
It is also of importance to note that all ions, regardless of whether or not they participate in the electrode reactions, are effective in carrying the current through the solution. Further, an uncharged particle, even though it may react at the electrodes, cannot contribute to the electrolytic conductivity.

A definite relationship exists between the amount of current passing through an electrolytic solution and the magnitude of chemical changes taking place at the electrodes. This relationship, known as Faraday's law, states that when 96,500 coulombs of electricity flow across a metal-electrolyte boundary, one gram-equivalent weight of a reacting substance will be oxidized

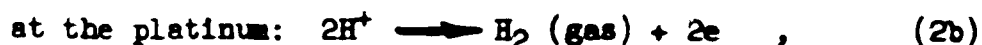
(or reduced). Thus, one ampere flowing through a solution of silver ions for 96,500 seconds will deposit 107.88 grams of silver at the cathode. The value, 96,500 coulombs per gram-equivalent, is known as the Faraday (F).

### PART III - INTERCONVERSION OF CHEMICAL AND ELECTRICAL ENERGY

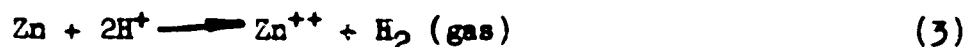
As an example of the release of chemical energy, consider the reaction which takes place when a piece of zinc metal is immersed in a solution of sulfuric acid, thus:



The reaction proceeds with the evolution of heat and work. By use of a galvanic cell, this reaction may be used as a source of electrical energy, as shown diagrammatically in Fig. 2. Here the zinc serves as one electrode, the chemically inert platinum as the other, in an electrolytic solution containing zinc sulfate and sulfuric acid. Now, when the two electrodes are externally connected, the reaction will take place as before, except that the hydrogen gas will be evolved at the platinum surface, and current will flow through the external circuit. The reactions occurring at the two electrodes will be:



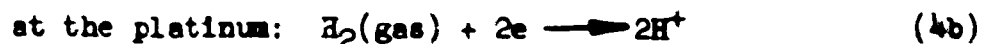
and the net chemical change will be:



which will be seen to be the same as the purely chemical reaction (1).

Now, by opening the external circuit and applying to the electrodes an increasing electromotive force of a polarity opposite to that of the galvanic cell, the electrochemical reactions 2a and 2b will proceed more and more slowly, and finally stop altogether. The exact value of the electromotive force required to stop the reactions is called the galvanic cell potential (E), and the electrical energy available from the cell is  $nEF$ , where  $n$  is the number of electrons involved in the cell reaction (in this case, two), and  $F$  the Faraday.

By increasing the external electromotive force still further, the electrode reactions may be made to proceed in the opposite direction, i.e.:



For this case, however, the platinum electrode must be surrounded by hydrogen gas, usually supplied by simply bubbling it over the surface. Here electrical energy is being converted into chemical energy, which can then be stored for future release of electrical energy.

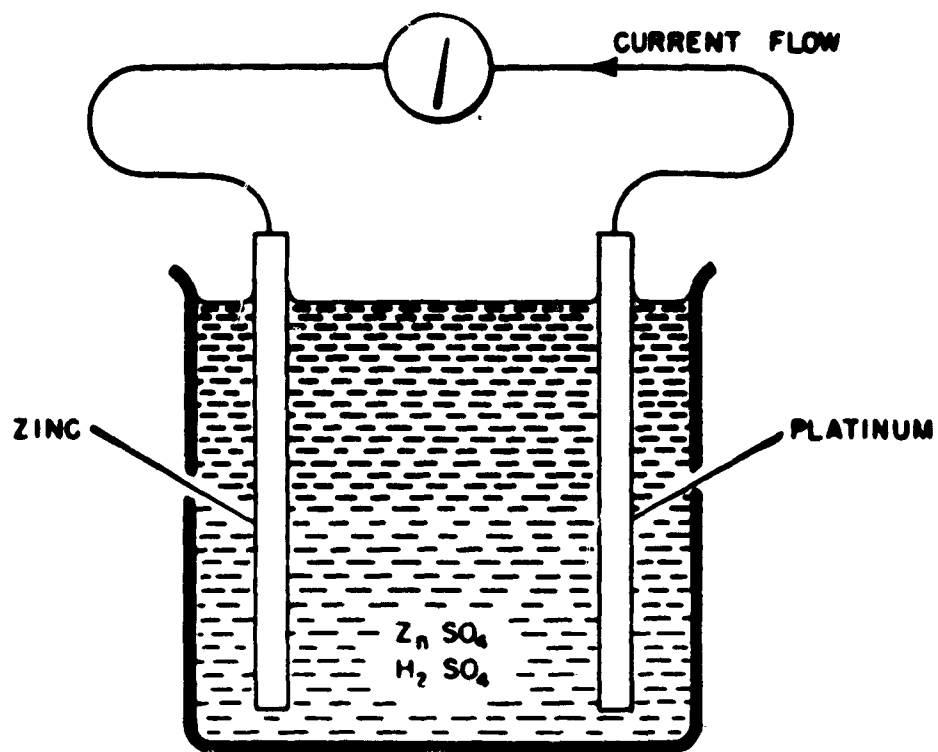


FIG. 2 - GALVANIC CELL AS SOURCE OF CURRENT

The value of the voltage obtainable from a galvanic cell is primarily a function of the nature of the reactions occurring at the electrodes. Thus, for this example, where zinc is dissolving and hydrogen is being evolved, the voltage is about 0.76. If the zinc and zinc sulfate are replaced by nickel and nickel sulfate, the voltage will be about 0.23. The difference in voltage developed by these two cells (0.76 as compared to 0.23) represents a difference in the tendencies for zinc to be oxidized to zinc ions and for nickel to be oxidized to nickel ions.

By using different combinations of many well-known electrode reactions, a large number of galvanic cells of this type may be constructed. Furthermore, it is possible to determine the voltages produced by any given cell from a knowledge of the thermodynamic quantities (energies) involved in the net chemical reaction occurring within the cell.

#### PART IV - ELECTRODES AND STANDARD ELECTRODE POTENTIALS

The voltage output of a given galvanic cell is a function of the tendencies of the two electrochemical reactions to take place at the electrode surfaces. Thus, a cell in which a strong oxidizing agent is reacting at one electrode and a strong reducing agent at the other has a higher voltage than a cell with a weak oxidizing agent and a weak reducing agent. Unfortunately, it is not possible to determine the fraction of the total cell voltage which should be attributed to each individual electrode. However, since we are interested only in potential differences, we may assign a potential to any individual electrode arbitrarily, then determine all others with respect to this one. This gives a series of single electrode potentials, the values of which are not absolute, but are consistent within themselves as to potential differences.

It will be remembered that each of the two galvanic cells cited as examples in Part III had as one of its electrodes a piece of platinum metal immersed in a solution containing hydrogen ions, with a stream of hydrogen gas bubbling over the metal surface. Since the reaction occurring at this electrode is the reduction of hydrogen ions to hydrogen gas (or, upon the reversal of current, the oxidation of hydrogen gas to hydrogen ions), it is called a hydrogen electrode. The tendency for this reaction to proceed in either direction varies somewhat with the concentrations of hydrogen ions and hydrogen gas at the electrode surface, so that in order to fix exactly the tendency for current to flow into (or out of) the electrode, it is necessary to fix these concentrations. When the effective concentration (activity) of the hydrogen ions is 1.0 Normal and the partial pressure of the hydrogen gas is 1.0 atmosphere, the electrode is referred to as a normal hydrogen electrode. This particular electrode has been adopted as the reference standard for all electrochemical systems, has been assigned an (arbitrary) potential of 0.0000 volts at all temperatures, and is somewhat analogous to the earth potential (ground) for the physicist.

The potential of any other electrode system is then defined as the E. M. F. which would be obtained from a cell consisting of the given electrode and a normal hydrogen electrode. If the components of the given electrode system are in what is referred to as their standard states, i.e., activities of solution

components 1.0 molar, partial pressures of gaseous components 1.0 atmosphere, solids a single pure substance, then the potential is the standard electrode potential.

The actual potential of an electrode changes from its standard potential according to the logarithm of the ratio of the activity of the products of the electrochemical reaction to the activity of the species reacting. Thus, for the hydrogen electrode:

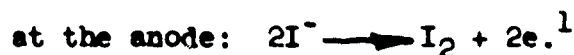
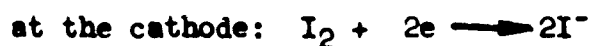
$$\text{actual potential} = \text{standard potential} - \frac{0.059}{2} \log \frac{(\text{partial pressure of H}_2 \text{ gas})}{(\text{activity of H}^+ \text{ ions})}$$

or, in general:

$$E = E_0 - \frac{0.059}{n} \log \frac{(\text{activity of products})}{(\text{activity of reactants})}$$

where  $n$  is the number of electrons involved in the reaction, and 0.059 is a constant.

From this equation, it can be shown how a galvanic potential can be obtained from two electrode systems identical in every respect other than the concentrations of the solution components. Consider the electrode system consisting of platinum metal immersed in a solution containing iodine and potassium iodide, a system which is used in several of the components of the electrolytic device. The reactions occurring at the cathode and anode in this case are:



If one electrode is surrounded by a concentration of iodine one hundred times as large as that around the other electrode, but both in the same concentration

of KI, then a potential difference of  $\frac{0.059}{2} \log 100$  (= 0.059 volts) will exist between them. The solutions may be separated from each other by a porous ceramic plate, which hinders only slightly the electrolytic conduction, but effectively prevents mixing of the solutions.

<sup>1</sup>

Because of a strong tendency of the neutral iodine molecule ( $\text{I}_2$ ) to associate itself with the negative iodine ion ( $\text{I}^-$ ), the actual reacting species is properly written  $\text{I}_3^-$ , and the equations as  $\text{I}_3^- + 2e \longrightarrow 3\text{I}^-$  or vice versa. However, as this association has no effect on either the operation of the mechanisms or the discussion here, the equations will be written as above to avoid confusion.



Conversely, it can be seen that if identical solutions are placed in both sides of such a divided cell, the application of an external voltage will transfer the iodine from one side to the other. That is, iodine will be reduced to iodide in the cathode side, and iodide oxidized to iodine in the anode side, such that substantially all the iodine will be transferred into the anode side. It is also important to point out that in a cell of this type, no net chemical change occurs in the solution, since the substance formed at one electrode is consumed in exactly equivalent amounts at the other. Local changes occur near the electrodes, and these give rise to currents and/or voltages, but no over-all chemical change takes place, so that the solution is not consumed, but will last indefinitely.

An electrode which can function like the iodine electrode described above, i.e., exactly equal but opposite chemical reactions for equal but opposite current flows, is called a reversible electrode. More precisely, a reversible electrode is defined as one for which the chemical reaction is exactly reversed by infinitesimal increases and decreases in an external E. M. F. about a point of zero current flow and no chemical reaction.

Reversible electrodes are of three types; at least one of each type is being used (or has been contemplated for use) in the electrolytic devices currently under development at NOL and DRL. The first type consists simply of a metal dipping into a solution of its ions; the silver/silver ion electrode of the osmotic cell is of this type. The second type consists of a metal in contact with one of its insoluble salts immersed in a solution of a soluble salt of the same anion. The silver/silver chloride in dilute potassium chloride is of this type, and was originally used in an osmotic cell described by patent disclosure "Functional Control of Fluid Flow by Use of Electro-Osmosis and Hydraulic Capacity and Resistance," Navy Case No. 16,912. The third type (commonly called a "redox" electrode) consists of an unattackable metal, usually platinum, immersed in a solution containing soluble forms of the same chemical in two different oxidation states. The iodine/iodide electrode system described above is of this type.

#### PART V - OVERVOLTAGE, POLARIZATION, AND POLAROGRAPHY

If the potential of an electrode in a galvanic cell is measured at the point of zero current flow, the value so obtained is called the reversible potential. Now if an increasing current is forced into (or out of) the electrode, a point will be reached at which the measured potential begins to change from the reversible potential. The value of current at which this occurs is a function primarily of the type of electrode and the area through which the current is flowing. The amount of this deviation (in volts) from the reversible potential is called the overvoltage, and the electrode in this condition is said to be polarized. Overvoltage results from the slowness of one or more of the processes occurring at the electrode, so that overvoltages are classified according to the nature of the slow process. The first type, activation overvoltage, results from the slowness of the chemical reaction itself; an example of this is encountered when sulfide is added to the electrolytic cell. The sulfide, which is absorbed on the platinum electrodes, "poisons" the cathodes

for the reduction of hydrogen ion, so that a high overvoltage for evolution of hydrogen is obtained, effectively preventing this interfering reaction. The second type, concentration overvoltage, results from the slowness of diffusion of the reacting species to the electrode surface, so that a concentration gradient arises near the electrode. Many of the electrochemical elements of the acoustic detector function through the concentration overvoltage of iodine at the cathode of these cells. This type of overvoltage is often referred to as concentration polarization.

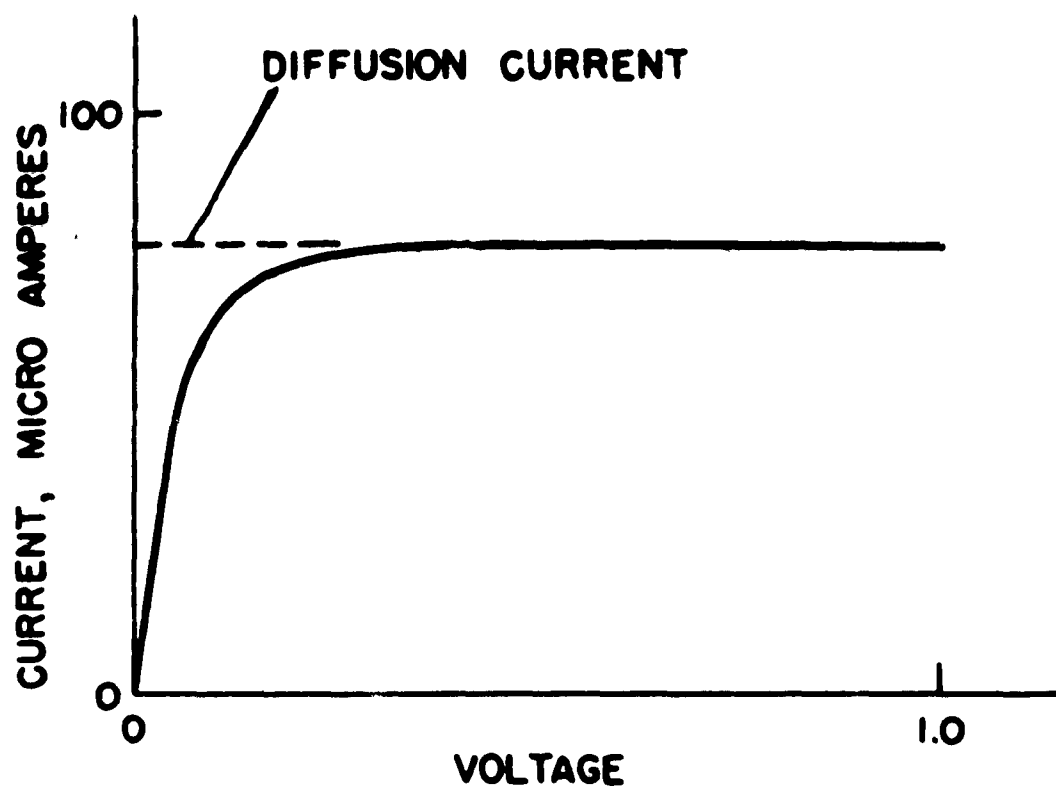
Another source of deviation from the zero current potential arises when, for any reason, an insoluble film forms over the electrode surface, thereby blocking the supply of reacting ions. This is sometimes called film overvoltage, although in reality it is of the nature of a pure resistance inserted in the circuit, with a consequent IR drop. This type of overvoltage was encountered in the acoustic electrolytic detectors, when insoluble metal hydroxide films formed on the cathode surface, with a resultant loss in sensitivity.

Because of the very important part played by concentration polarization in the electrolytic mechanisms, it will be described in somewhat greater detail. Consider a cell consisting of two pieces of platinum immersed in a solution containing iodine and potassium iodide. If there are no differences in concentration through the solution, each piece of platinum will be at the same value of potential, so that if they are externally connected, no current will flow. However, if an external source of E. M. F. is applied to the electrodes, the system becomes an electrolysis cell, and current will flow with the reduction of iodine at the negative electrode (cathode) and the oxidation of iodide at the anode. The value of the current at any given value of applied E. M. F. is controlled by one of the following three factors, assuming no activation or film overvoltage:

- (a) Electrolytic resistance through the solution.
- (b) Supply of iodide ion to the anode.
- (c) Supply of iodine to the cathode.

By adding a large excess of potassium iodide to the solution and using a large area anode, effects (a) and (b) may be minimized, so that the current will be regulated solely by the supply of iodine to the cathode. In a quiescent solution the rate at which iodine reaches the cathode is governed by a diffusion process, the laws of which are well known. A plot of current vs voltage for such a system is shown in Fig. 3. The value of current on the flat portion of the curve is called the diffusion or limiting current, and is proportional to the area of the electrode, the concentration of iodine in the solution, and the diffusion "coefficient" of the iodine.

Diffusion currents can be obtained for a large number of chemical species in addition to iodine, and since the diffusion current is proportional to the concentration of the species, this has been made the basis of an analytical technique called polarography. Furthermore, the value of the electrode potential at which the species is reduced depends upon the known standard electrode



**FIG. 3 - TYPICAL CURRENT - VOLTAGE CURVE FOR CONCENTRATION POLARIZATION**

potential of that species, so that a qualitative as well as a quantitative analysis can be obtained from a single current-voltage curve.

If more than one of the chemical species in a solution are capable of being reduced at a given potential, then both (or all) reductions will proceed simultaneously when that potential is reached. See, for example, Fig. 4, which is a current-voltage curve for an iodine-iodide cell containing dissolved oxygen. The oxygen reaction in this case is not reversible (nor is the later evolution of hydrogen), so that the only reaction occurring at the anode is oxidation of iodide to iodine, not balanced by an equivalent reduction of iodine at the cathode. The end result is a gradual increase in iodine concentration, and it is for this reason that oxygen must be excluded from the cell, and the hydrogen evolution reaction prevented.

The manner in which concentration polarization is used in a fluid flow detector is simple. Since the value of current is controlled by the rate at which iodine reaches the cathode, the current increases when the supply of iodine to the cathode is increased. This is accomplished by either disturbing the solution, thereby upsetting the diffusion layer, or by pumping a concentrated iodine solution over a cathode surrounded by a dilute solution. In a flow detector, the solution is "disturbed" (forced back and forth through a cathode in the shape of an orifice) by the fluid flow that one desires to detect. In a d.c. flow detector a concentrated solution is "pumped" over a cathode. In the derivative devices and product devices, the pumping is accomplished by means of another electrolytic unit, the osmotic cell.

#### PART VI - ELECTROKINETIC PHENOMENA AND THE ELECTRO-OSMOTIC CELL

At the boundary of a solid and a solution, there exists a distribution of charged particles (ions) called the electrical double layer. Using a glass surface in contact with a dilute water solution as an example, this ionic distribution arises as follows: Due to unbalanced electrical forces, the glass surface possesses a net negative charge, to which the positive ions in solution are attracted. The large majority of these positive ions are tightly bound to the surface; that is, they are no longer free to move relative to the solid. However, a small percentage of these ions are distributed a bit further into the solution than are the fixed ions, and are movable with respect to the solid (Fig. 5(a)). Note that this double layer of charge distribution is analogous to a charged parallel plate condenser, and many of the theoretical calculations on double layer effects are made on this basis. However, the potential drop perpendicular to the surface of the solid is not as sharp and well defined as in the parallel plate condenser (Fig. 5(b)), but tails off into the solution through the region of movable ions. The potential drop through this region is called the zeta ( $\zeta$ ) potential, and it is with this potential that all electrokinetic phenomena are concerned. For this discussion, it is of most importance to remember that a certain portion of solution, movable with respect to the solid, contains (in this case), a net positive charge. In electrokinetic experiments, the region containing this net charge must be made a significant fraction of the total solution. This is accomplished by means of capillary tubes (large surface to volume ratio), or by fritted glass discs, which are

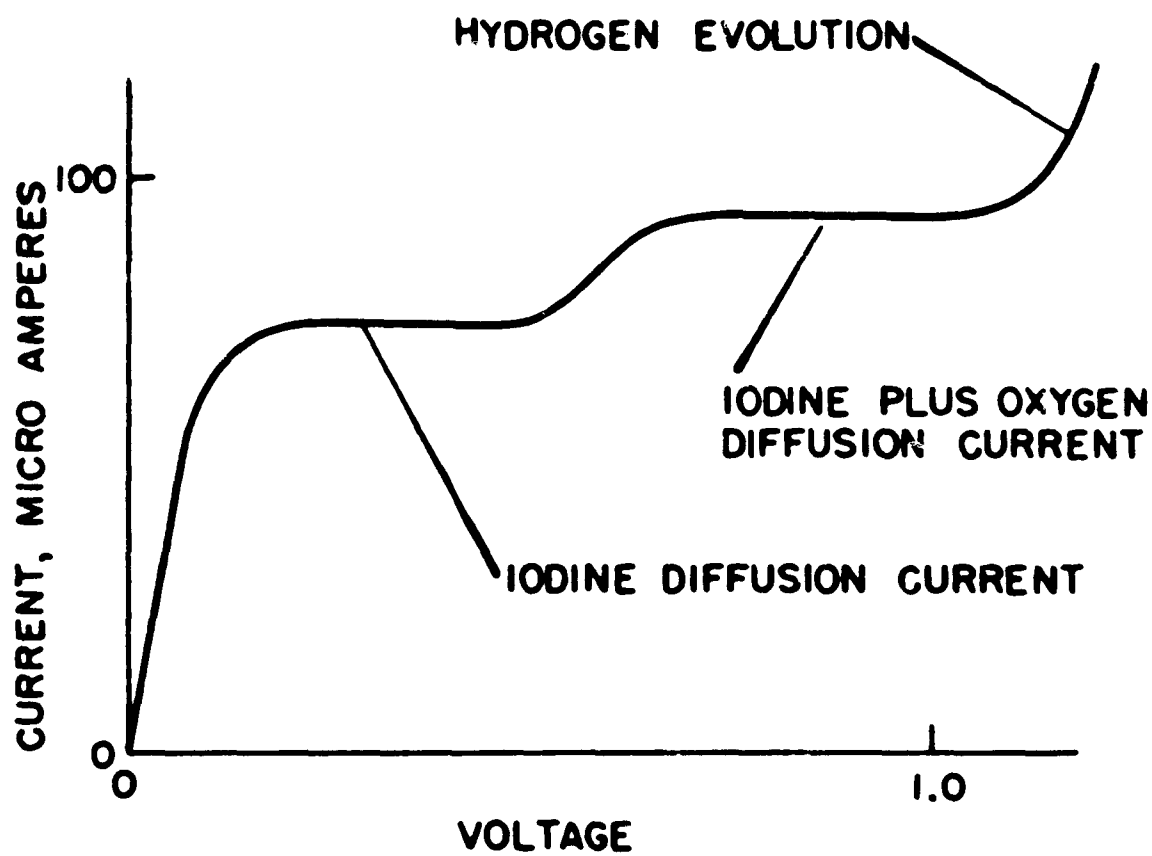


FIG. 4 - TYPICAL CURRENT-VOLTAGE CURVE FOR IODINE-IODIDE CELL CONTAINING OXYGEN

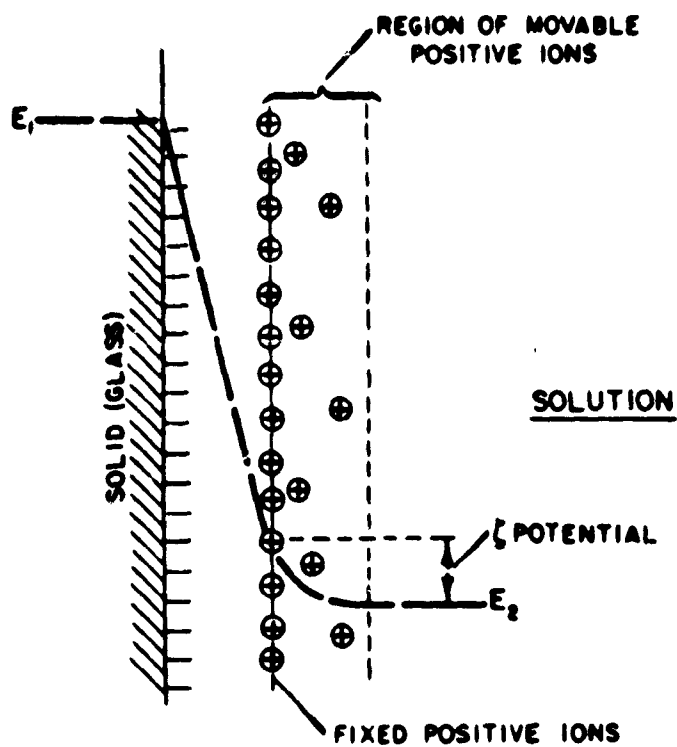


FIG. 5(a) - POTENTIAL DROP AND CHARGE DISTRIBUTION  
IN THE ELECTRICAL DOUBLE LAYER

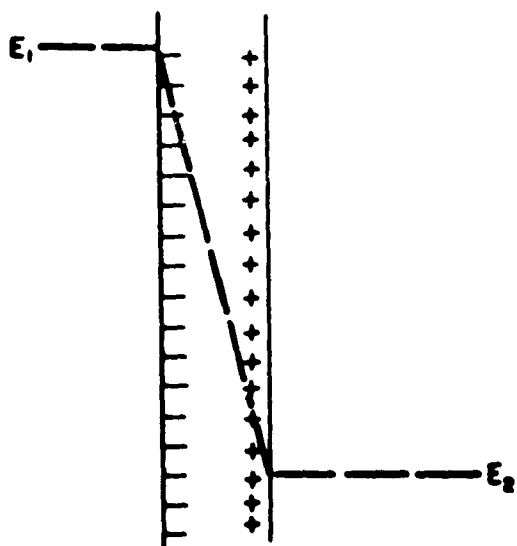


FIG. 5(b) - POTENTIAL DROP AND CHARGE DISTRIBUTION  
IN PARALLEL PLATE CONDENSER

nothing more than a large number of irregularly shaped capillary tubes in parallel.

In Figure 6 an electrical double layer is shown on the inside of a glass capillary tube, with electrodes placed at the ends of the tube. Note that if (as in Figure 6(a)) the fluid is forced through the tube by means of an applied hydraulic pressure, the region containing excess positive charges will be carried along, creating a potential drop from one end of the tube to the other. This phenomenon is called streaming potential, and the magnitude of the streaming potential is directly proportional to the applied hydraulic pressure.

Conversely, if instead of an external hydraulic pressure, an external potential is applied to the two electrodes, the solution will be carried down the tube toward the negative electrode by the movement of the excess positive ions (Fig. 6(b)). This movement of fluid under the influence of an applied voltage is called electro-osmosis. If the fluid is allowed to flow freely through the tube, the rate of flow will be directly proportional to the applied voltage; if the fluid flow is restrained, then hydraulic pressure will be developed across the tube, and the value of this pressure will be directly proportional to the applied voltage.

The flow rates and pressures obtainable at around one volt applied potential across a fritted disc are rather small, in the range of  $10^{-5}$  to  $10^{-5}$  cubic centimeters per second for flow rates, and 5 to 10 centimeters of water in the case of pressure build-up.

Of these two phenomena, the only one of interest here is electro-osmosis, which is used to make the low-voltage fluid pump employed in the derivative and product units.

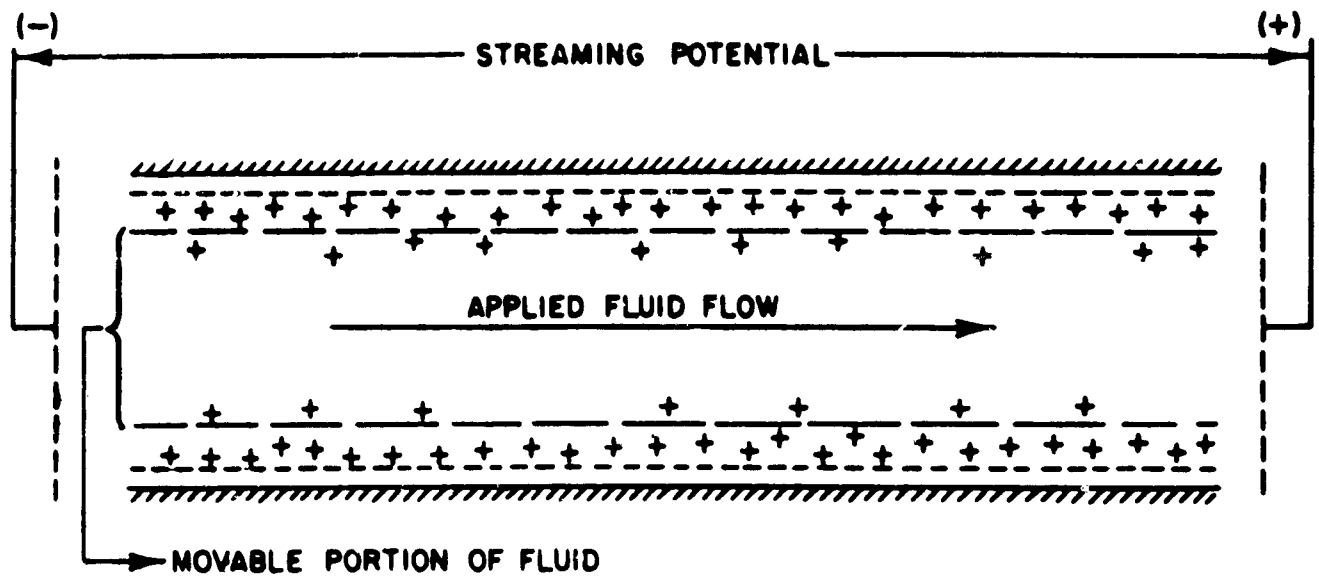


FIG. 6(a) - ORIGIN OF STREAMING POTENTIAL

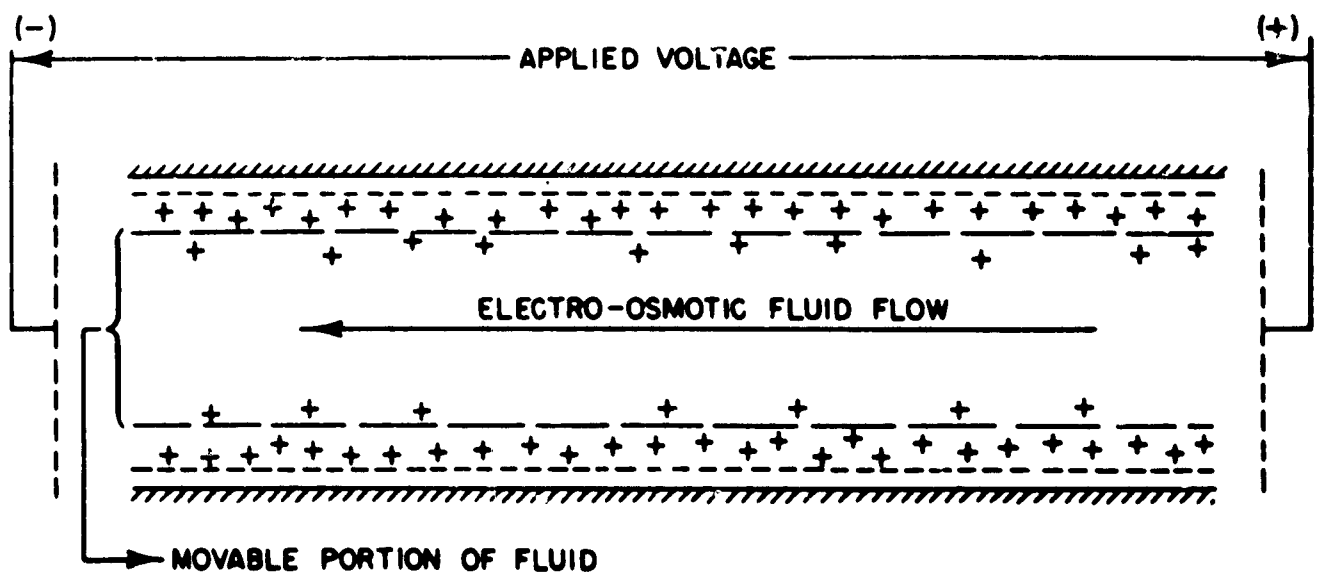


FIG. 6(b) - ORIGIN OF ELECTRO-OSMOSIS



PRINCIPLES OF VERY LOW POWER ELECTROCHEMICAL DEVICES<sup>†</sup>

by

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This paper presents some of the fundamental principles of a new technology which utilizes the control of electrons moving in solution, rather than in a gas or vacuum as in electron tubes, or in a solid as in transistors. During the past six years many of the technical details of this new technology utilizing the flow of electrons in solution have been worked out at Defense Research Laboratory in cooperation with Mr. N. N. Estes and his staff at U. S. Naval Ordnance Laboratory, White Oak, Maryland.

The principal advantage of these new devices over previous ones lies in their very low power consumption, much less, for example, than that required to operate a comparable transistor system. Other advantages are inherent stability, long life, ease of manufacture, and simplicity of operation. Their principal disadvantage is the limited frequency range over which they are operable, presently lying between 0 and 200 cps.

The component parts of these new systems vary widely in the type of function performed; there are, for example, elements for detecting and metering both dc and ac fluid flows, or dc and low frequency ac electrical signals; units for taking logarithms, derivatives, and products of electrical and/or fluid flow inputs; units for integrating pressures, flows or electrical signals over short intervals of time, etc. The operation of all these units is based upon fundamental and well known electrochemical phenomena, so they may be referred to as electrochemical units.

As far as is known, at Defense Research Laboratory and Naval Ordnance Laboratory, the idea of using an electrolytic cell for acoustic detection was first proposed in 1941 by D. S. Muzzey, presently of NOL, who was working at that time at the Geophysical Laboratory of the Shell Oil Company. Very early detectors which worked after a fashion were tried at that Laboratory, and then offered to the Navy. Various models were constructed at NOL between 1942 and 1944, but the program was dropped because of the variability between units. At present enough research has been carried out to understand the reasons for

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<sup>†</sup>Research on this subject was supported under U. S. Navy, Bureau of Ordnance Contract NOrd-10639 and Contract NOrd-16382.

variability between units and to be able to control the characteristics of the units.

The object of the present paper is to outline the principles of operation and to describe briefly some of the specialized electrochemical and acoustical research which was necessary in the development of these devices. Subsequent papers in this and other journals will describe construction details and performance characteristics.

#### Use of Concentration Polarization for Flow Detection

The use of platinum electrodes and the diffusion current between them to analyze a solution of electrolytically reducible or oxidizable substances is well known. Also, a great deal of information on the increase of current between electrodes with agitation of the solution has been published and it has been established that the current between electrodes is a function of the fluid flow between them. This paper will show some of the means for controlling the function of the output current with relation to the fluid flow. Linear or logarithmic current outputs as a function of flow may be obtained by changes in the electrode design.

A typical flow detector is shown in Figure 1. Electrodes may be of any metal which is inert to the electrolytic system used. In this particular example platinum electrodes are used in an electrolytic system of iodine and potassium iodide in water. The cathodic reduction of iodine is made the controlling reaction by using a low concentration of iodine ( $10^{-2}$  N) and a high KI (supporting electrolyte) concentration (0.5 N).

At the electrodes the following reactions occur:

- (1) at the cathode  $I_2 + 2e \rightleftharpoons 2I^-$
- (2) at the anode  $3I^- \rightleftharpoons I_3^- + 2e$

The current in the system is evidently controlled by the number of  $I_3^-$  ions which come into contact with the cathode. When there is no electrolyte flow through the cathode orifice, the current is controlled by diffusion; fluid flow of the electrolyte increases the number of available  $I_3^-$  ions at the cathode and the current in the system increases. It should be noted that the reactions within the detector are reversible and there is no depletion of the unit during the chemical processes. Other electrolyte systems may be used, as, for example, ferricyanide-ferrocyanide, bromine-bromide, ceric-cerous, ferric-ferrous, etc. It is only necessary that they be reversible redox systems.

Current voltage curves for a cell of this type are shown in Figure 2 for different values of low frequency acoustic energy incident on the diaphragm. A plot of the equilibrium current as a function of the incident pressure is given in Figure 3. The relationship between current and pressure is expressed by equations of the type:

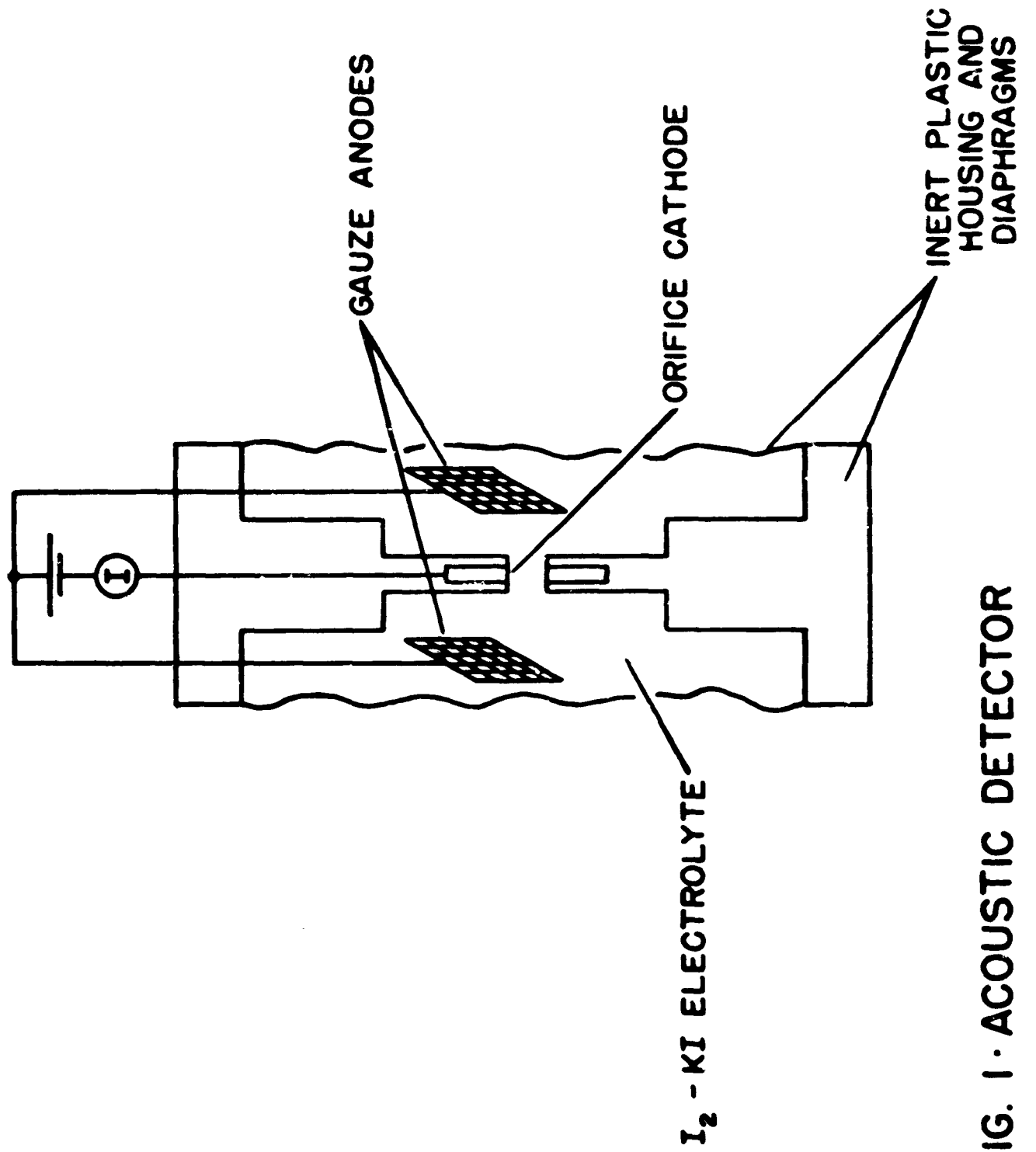
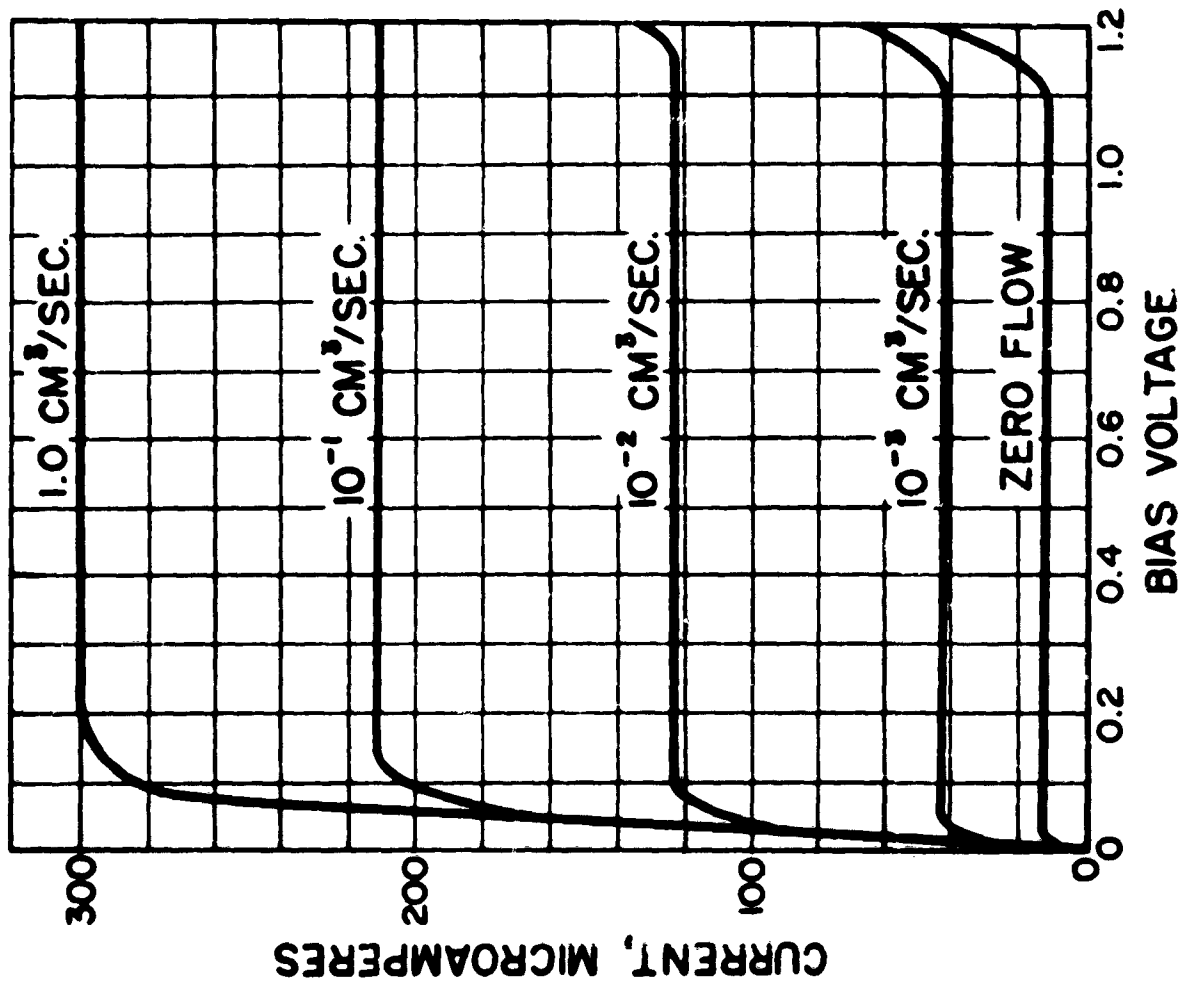


FIG. 1 - ACOUSTIC DETECTOR

FIG. 2. CURRENT - VOLTAGE  
CURVES FOR VARYING  
SINUSOIDAL FLOWS IN  
ACOUSTIC DETECTOR



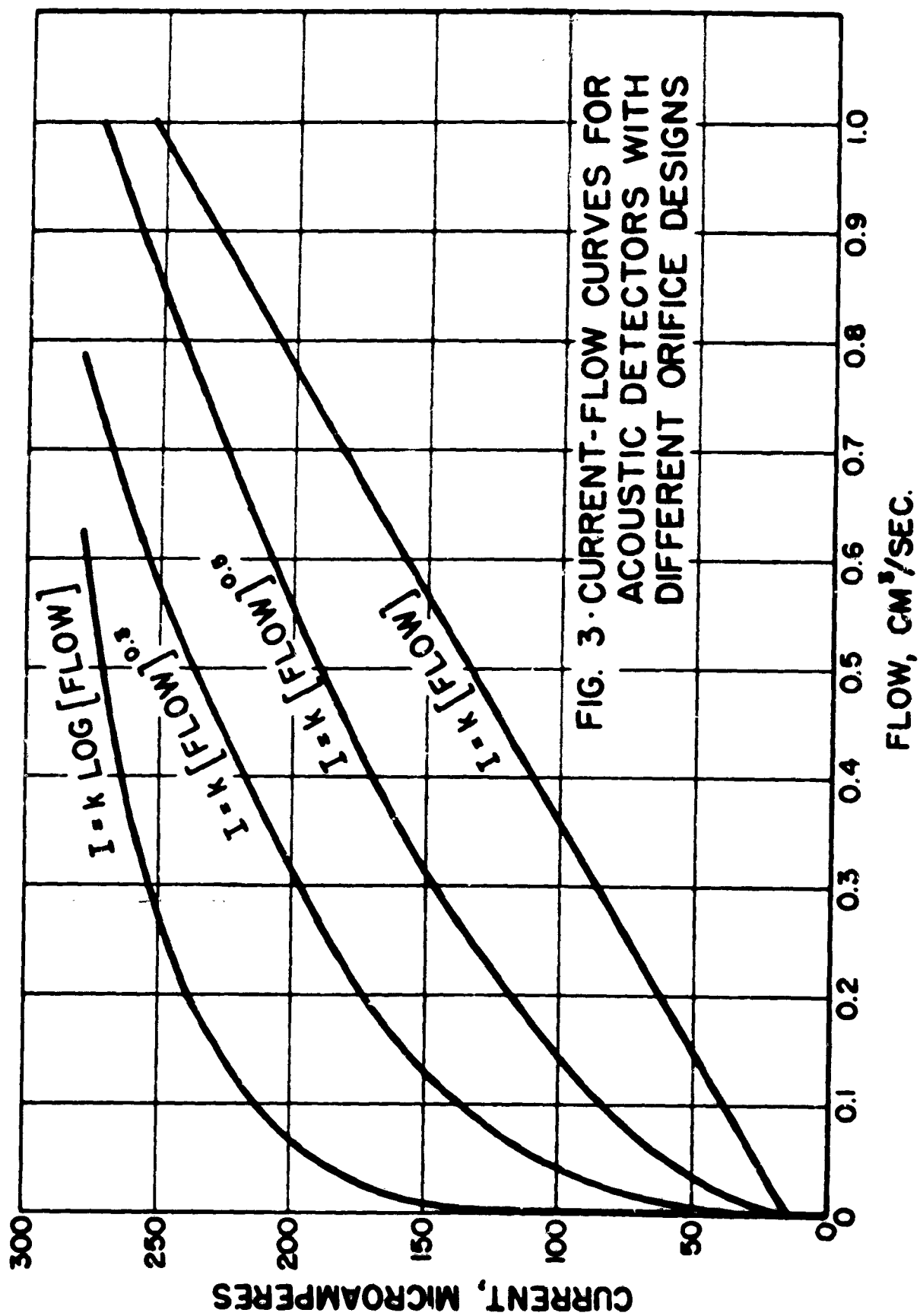


FIG. 3-CURRENT-FLOW CURVES FOR ACOUSTIC DETECTORS WITH DIFFERENT ORIFICE DESIGNS

$$I = k P^n \quad \text{or}$$

$$I = k \log P,$$

with the values of  $n$  and  $k$  dependent on the geometry of the cathode.

Figure 4 shows the type of response which may be obtained from a detector system with an electrode geometry which yields a logarithmic current output with respect to acceleration of the electrolyte. A range of three decades in acceleration is achieved by a very simple instrument consisting of an electrochemical detector, a battery, and a microammeter. The units used for obtaining the data shown in Figure 4 are pictured in Figure 5. Note that no switches or other controls are used to cover the three decades of acceleration from  $1 \text{ cm/sec}^2$  to  $10,000 \text{ cm/sec}^2$ ; the acceleration may be calibrated directly on the meter face. Figure 6 shows the preliminary model of the accelerometer used in obtaining the data shown in Figure 4.

This particular unit was tuned to resonate at 30 cps as shown in the frequency response curve of Figure 7, but these units actually have their best response below 30 cycles down to dc. Particularly good results may be obtained between 2 cps and 10 cps.

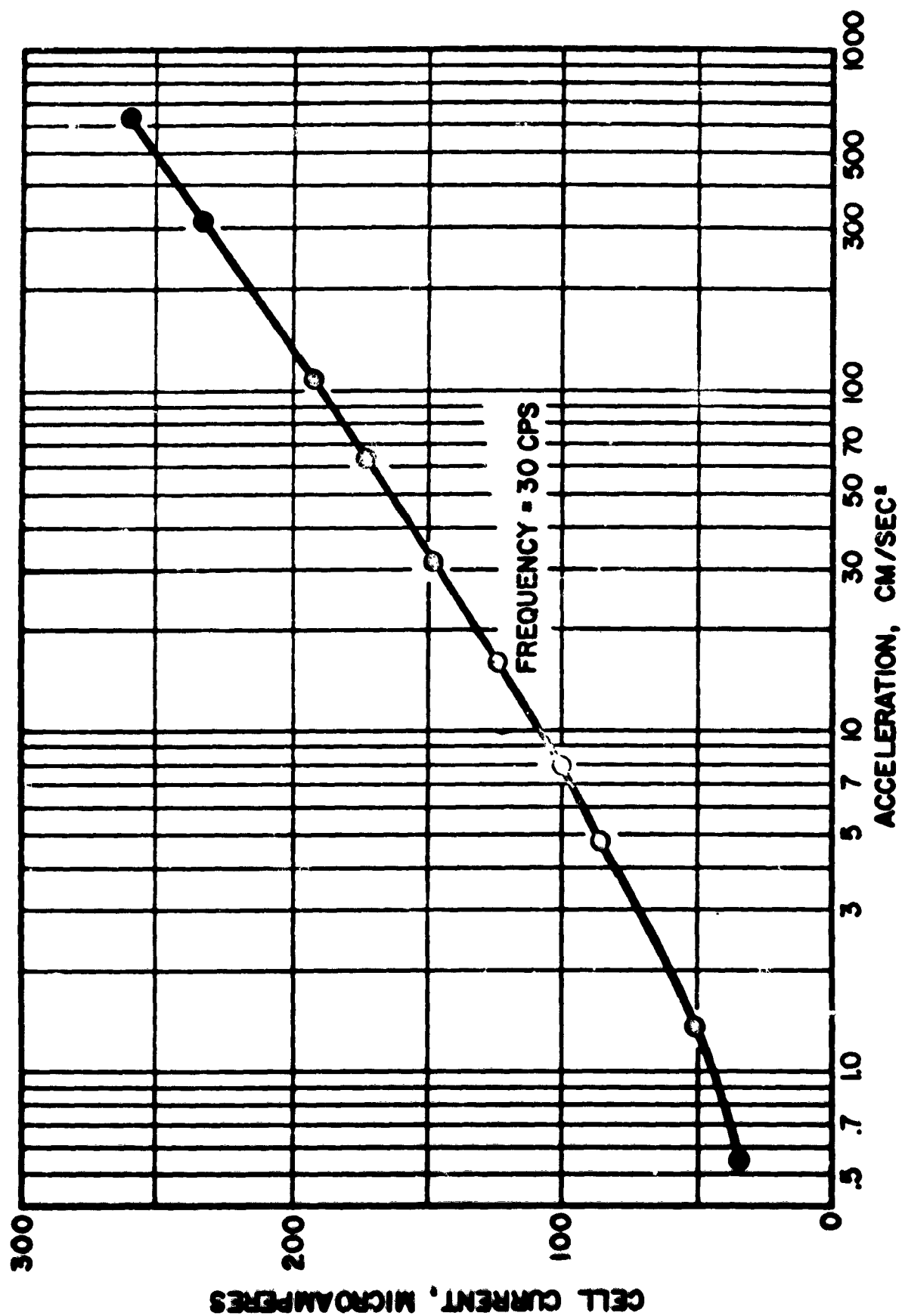
From an electrochemical standpoint, the proper operation of these units requires the following:

1. As nearly reversible electrode reactions as possible, so that no energy is consumed in overcoming activation polarization.
2. Equal and opposite reactions occurring at the anode and cathode; i.e., a redox system, so that no net changes in concentration take place as current flows through the cell.
3. Absence of reducible or oxidizable impurities. A reducible impurity not only yields a momentarily higher current, but builds up a permanent higher concentration of the primary reducible reactant (in this example, iodine) by the increased anodic oxidation.

#### The Separated Detector for DC Measurements

The cell described above was designed primarily for detection and metering of acoustic energy (ac pressures). A more satisfactory design for dc flows and pressures is shown in Figure 8. In this cell an additional cathode is placed in the right hand compartment so that the bias voltage transfers the iodine from this side to the anode side, resulting in a final concentration of virtually zero in the cathode side.

The working cathode consists of a small piece of closely woven platinum gauze situated in an orifice between the two compartments. Flow from left to right (concentrated to dilute) produces an electrical signal directly proportional to the magnitude of the flow. For a detector operating linearly,



**CALIBRATION OF ELECTROLYTIC CELL NO. BG722B387 AS AN  
ACCELEROMETER. MOTION APPLIED ALONG AXIS OF  
CYLINDRICAL SYMMETRY**

**Fig. 4**

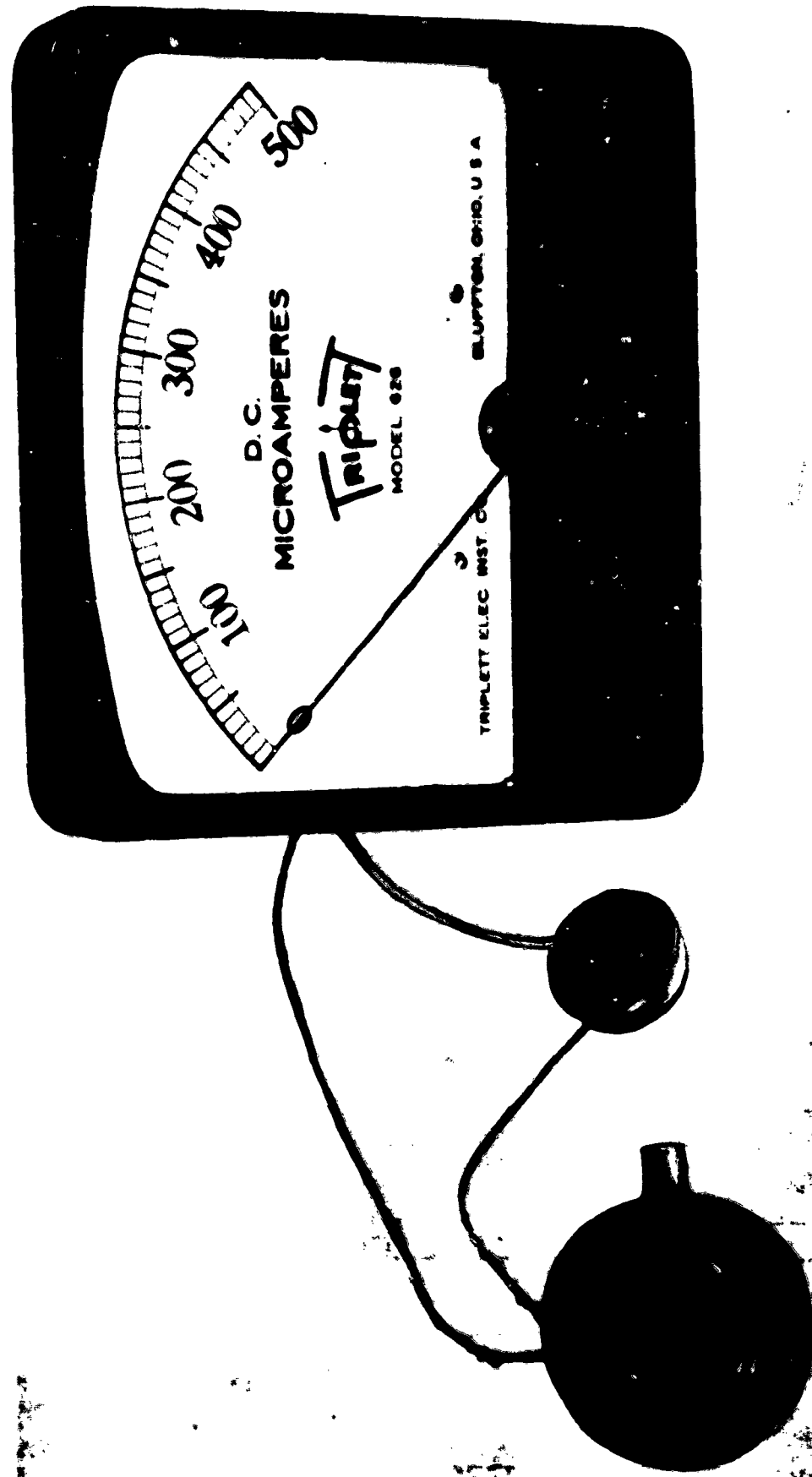
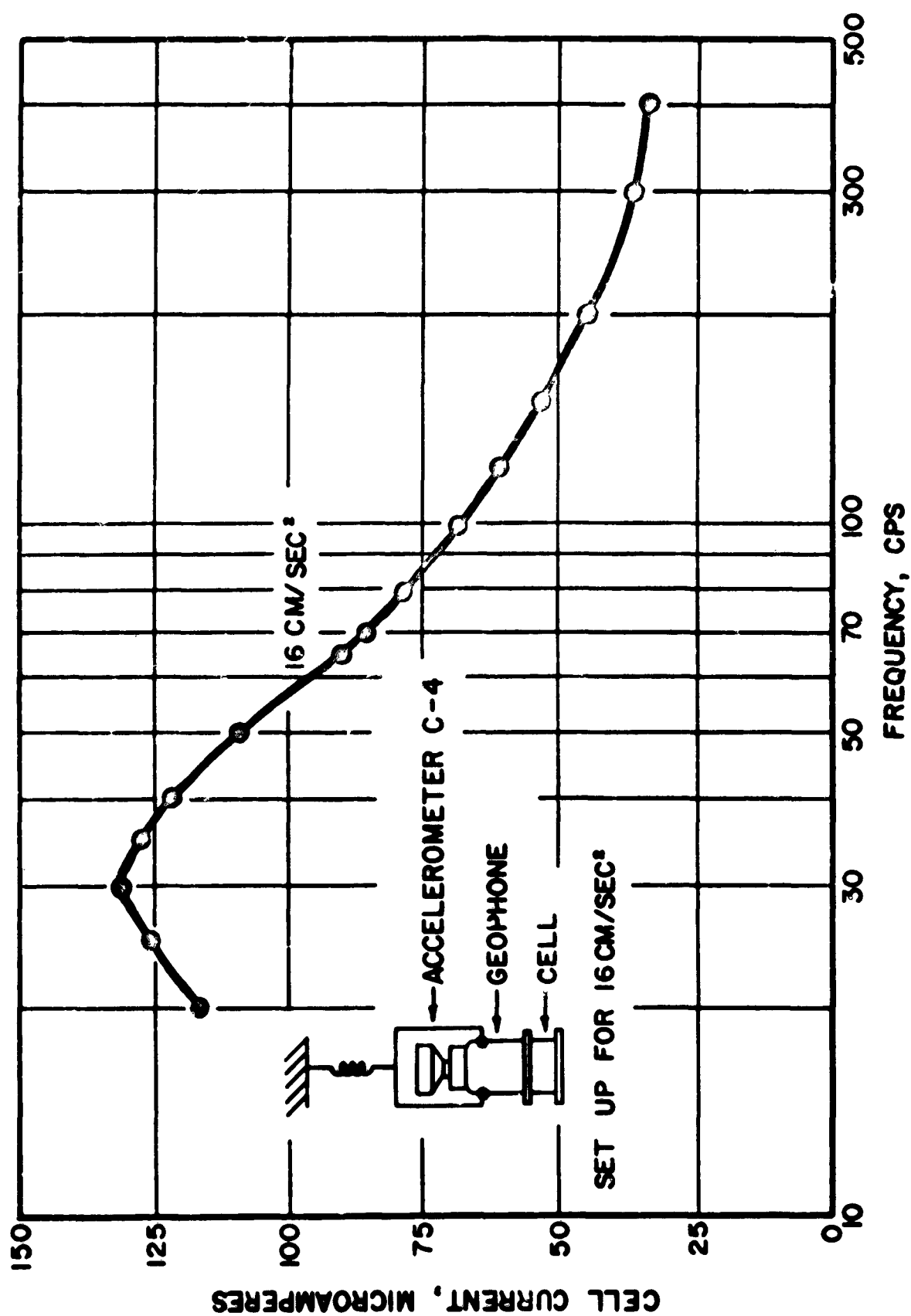


FIG. 5





FIG. 6



**Fig. 7**

**FREQUENCY RESPONSE OF ELECTROLYTIC CELL NO. BG722B387 AS AN ACCELEROMETER. MOTION WAS APPLIED ALONG THE AXIS OF CYLINDRICAL SYMMETRY**

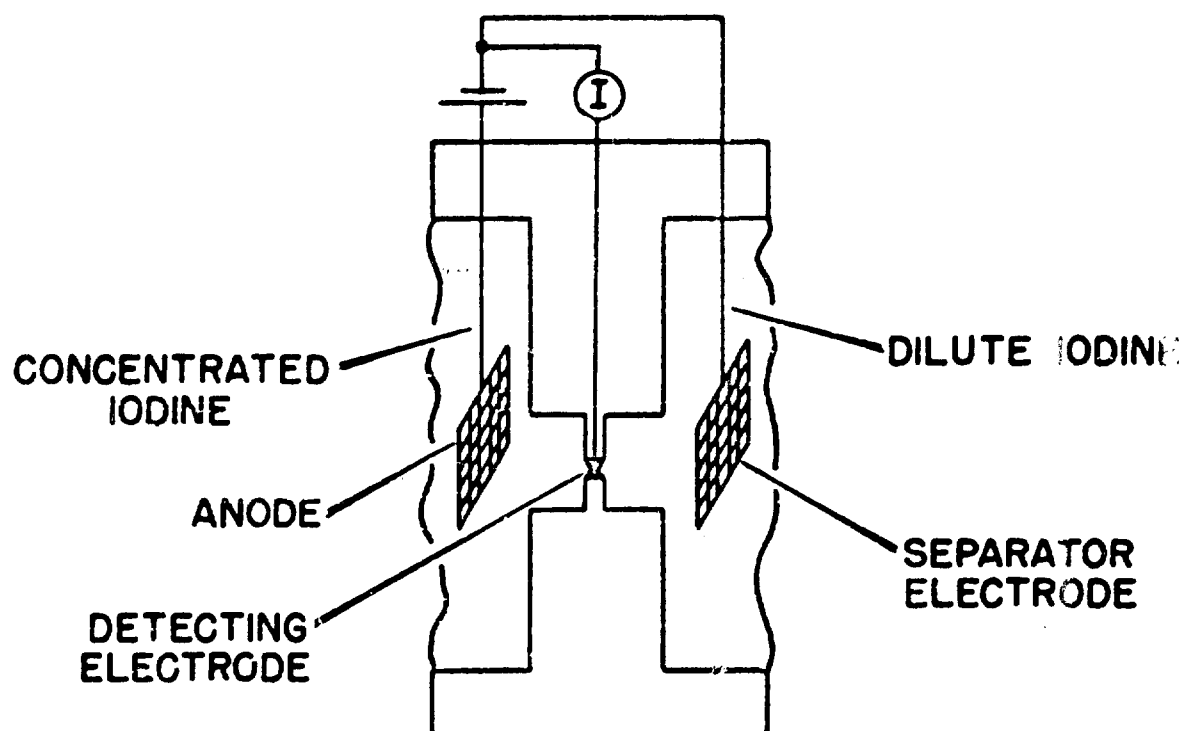


FIG. 8 · SEPARATED DETECTOR

i. e., reducing all the iodine in the fluid flowing through the gauze, the current output is given by the equation:

$$I = 10^{-3} F N \frac{dv}{dt}$$

where

F = the Faraday

N = normality of the reducible substance  
on the anode side

$\frac{dv}{dt}$  = flow rate in cm<sup>3</sup>/sec.

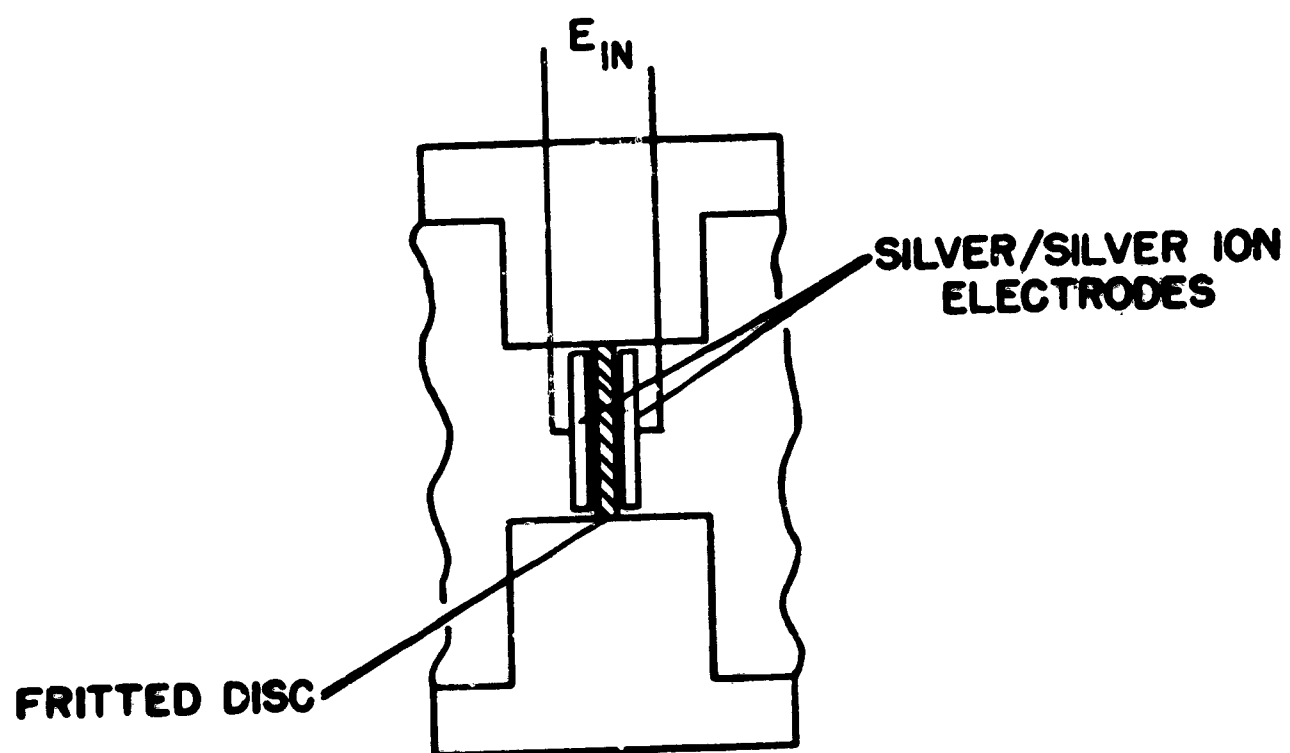
From this equation, assuming iodine normality of 10<sup>-1</sup>, it can be seen that flow rates as low as 10<sup>-5</sup> cm<sup>3</sup>/sec yield currents in the neighborhood of 100 microamperes, or some ten times the no-flow current. Experiments have shown that, by suitable design of the detecting cathode, linear current outputs are obtainable over a range of four orders of magnitude in the flow rates.

Note that the unit shown in Figure 8 is also a rectifier, in that fluid flow from right to left will not produce a current, since no iodine is carried over the detector gauze. A full-wave detector may easily be constructed by using two anode compartments and two detector gauzes.

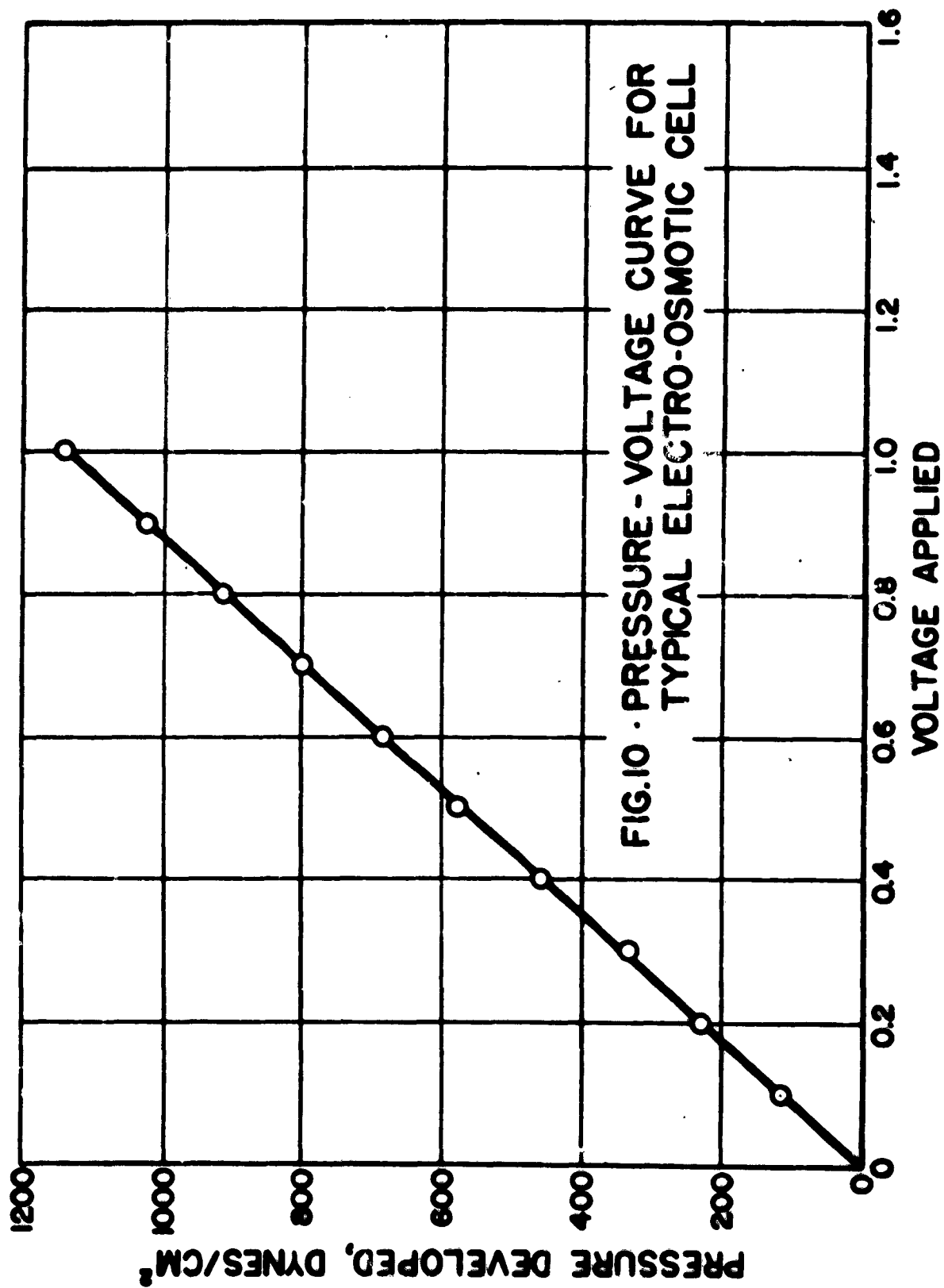
#### Conversion of Electrical Energy to Fluid Flow

In order to perform various mathematical operations upon the output currents of the devices described above, it is necessary to have a unit which carries out the reverse operation of converting these very low power electrical signals into fluid flows. In this manner, electrical and fluid flow signals may be fed from unit to unit in much the same manner that currents and voltages are fed through electronic networks. In addition to simple amplification, several mathematical operations may be carried out upon the original incident signal or signals in this manner; for example, products, ratios, derivatives, etc., may be obtained.

The simplest and most reliable method of carrying out this reverse effect is by the use of electro-osmosis. An electro-osmotic cell (Figure 9) consists of a fritted glass disc dividing a cell into two compartments, with electrodes on each face of the disc. The operating characteristics of such a cell can be made to vary over extremely wide ranges by control of such variables as disc porosity, thickness, and diameter, and choice of working liquid. The important point, however, is that the fluid flow produced by an applied voltage is linear with the value of voltage. If the flow is restrained, as, for example, by means of the plastic diaphragms of Figure 9, then the electro-osmotic pressure developed is linear with the voltage. In Figure 10 the equilibrium pressures for a typical "fine" porosity disc (about 4.0 microns pore diameter) is shown plotted as a function of applied voltage, using distilled water as the working fluid. Unrestrained fluid flow for a 30 mm diameter, 20 mm thick disc of this



**FIG. 9 · ELECTRO-OSMOTIC CELL**



type is in the neighborhood of  $10^{-3}$  cm<sup>3</sup>/sec at 1.0 volt applied to the electrodes. It will be remembered that a flow rate of  $10^{-5}$  cm<sup>3</sup>/sec through a separated detector will yield some 100 microamperes output, so that the values of flow rate produced by the electro-osmotic cell easily cover the working range of the other electrochemical units.

An idea of the power gains obtainable with these electrochemical units may be illustrated by combining the electro-osmotic cell with a linearly operating separated detector. The current drawn by the electro-osmotic cell at 1.0 volt applied can be held to about 30 microamperes if the working fluid has a conductivity of some  $10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>, giving a power input of 30 microwatts. The linear detector coupled to the cell can be designed to give an output of 10 milliamperes dropped across a load resistor of 100 ohms, or a power output of 10 milliwatts. This represents a power gain of some 330 fold; this could easily be increased by an additional order of magnitude.

One of the essential requirements of a properly operating electro-osmotic cell is that the working electrodes polarize as little as possible. For alternating current signals this is no particular problem, but for continuous and uni-directional dc signals, suitable electrodes are not so easily found. To date, the most satisfactory electrodes have been the simple metal/metal-ion type, particularly Ag/Ag<sup>+</sup> made by firing compressed tablets of Ag<sub>2</sub>O.

Another method of obtaining the conversion of electrical energy into flow energy is through the use of the electro-capillary curve of mercury. This has not been studied as thoroughly as has the electro-osmotic cell, but its workability has been demonstrated. The most interesting thing about the electro-capillary curve is the fact that the surface tension (and thus the fluid displacement) varies as the square of the voltage applied to the interface. Furthermore, because of the extremely low currents required to charge the mercury double layer, and the relatively large displacements obtainable by the changes in surface tension, the power gain through such a system can be higher even than the examples cited above.

#### Use of Anodically Deposited Iodine

The last aspect of these electrochemical devices to be described in this paper is the use of a reducible substance (iodine) formed in place by the passage of anodic current through the electrolyte solution. For example, Figure 11 shows an anode and cathode separated by a small volume containing KI only. Other cathodes are shown at the ends of this "corridor," through which the fluid is free to flow. Now, obviously, since there is no iodine inside the corridor, no current is obtained at the end electrodes, regardless of the fluid flow. If, however, an external current is passed across the corridor pieces, iodine will be formed at the anode of the corridor, which will then either diffuse across to the cathode, or may be forced to either of the detector gauges by fluid flow.

The iodine thus generated, and subsequently reduced at any of the three cathodes shown, may then be returned to the anode again and again, with the

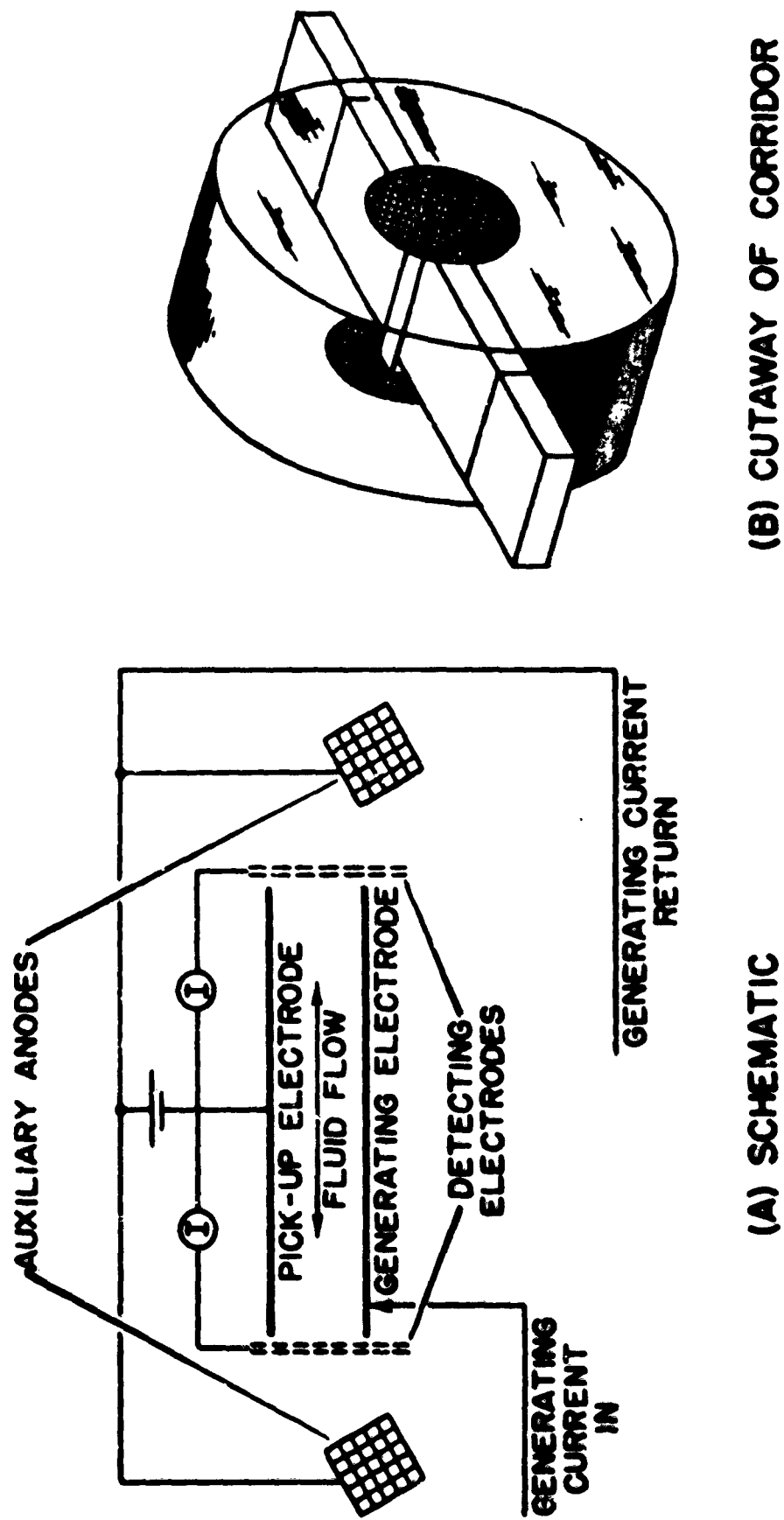


FIG. 11 · ELECTRODE ARRANGEMENT FOR USING  
ANODICALLY DEPOSITED IODINE



result that a small, steadily applied generating current builds up into a larger and larger cathodic current, which can, at a preselected point, be shunted to another part of the cell, thus returning the corridor to its initial "iodine-free" condition.

By the use of the principles just described, operations such as multiplication and integration may be carried out. Obviously, the ramifications and possibilities of these electrode arrangements are numerous.

#### Summary

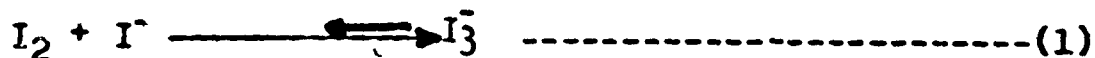
The method in which several common electrochemical phenomena have been combined to yield a new technology for very low power detection and control devices has been described. The operation of a few of the many possible units has been described, and some of the characteristics cited to show the operating ranges, low power requirements, and power gains obtainable. Some of the electrochemical requirements of properly operating cells have also been mentioned. Further details on the operation of the units and of the research which has been done to bring them to the present state of development will be revealed in subsequent papers in this and other journals.

## BASIC PRINCIPLES OF ELECTROCHEMICAL INTEGRATORS

By Herbert B. Reed  
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A reversible, chemical oxidation-reduction system (redox system), such as an aqueous solution of iodine and potassium iodide, can be used under certain conditions to measure the concentration of one component -- in this case the iodine. Because of this property, and because the system is essentially reversible, an electrochemical integrator can be made. Let us examine the iodine-iodide system in more detail. First, let us see how concentrations can be measured.

Iodine, when it is dissolved in an aqueous solution of potassium iodide, exists predominantly as the triiodide ion:



The solution is composed predominantly of triiodide ions ( $I_3^-$ ), potassium ions ( $K^+$ ), iodide ions ( $I^-$ ), and water molecules ( $H_2O$ ), with small amounts of molecular iodine ( $I_2$ ), hydrogen ions ( $H^+$ ), and hydroxyl ions ( $OH^-$ ).

Consider such a solution which possesses a small value for the ratio of triiodide ion concentration to iodide ion concentration.  $\left( \frac{a_{I_3^-}}{a_{I^-}} \right)$ . Consider also an experiment in which this

solution is electrolyzed between noble metal (Platinum) electrodes under an inert atmosphere (such as nitrogen) in equipment such as that shown in figure 1. Simultaneous readings of the steady state currents and voltages are taken for various values of the applied voltage. A plot of the steady state cathodic current density versus the applied voltage will be as shown in figure 2 for several values of triiodide ion concentration at a given temperature in quiescent conditions. The voltage independent portion of this curve is called the limiting ("diffusion") current. A plot of the limiting current density versus the triiodide ion concentration is shown in figure 3 for several temperatures for a quiescent system. For a given set of conditions, these curves are stable in time. There is no net generation or depletion of triiodide ions, for the system undergoes the following "reversible" electrochemical reactions:

a. At the cathode:



b. At the anode:



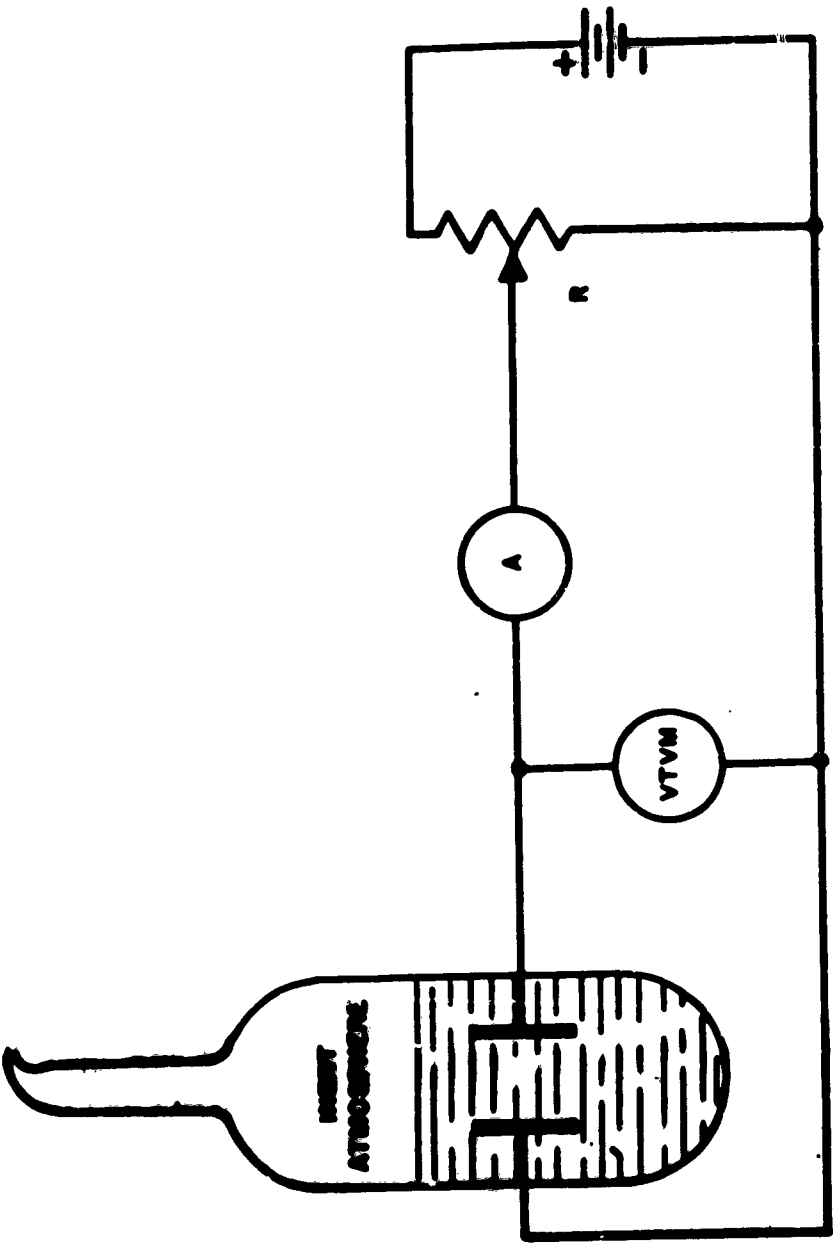


FIG. 1

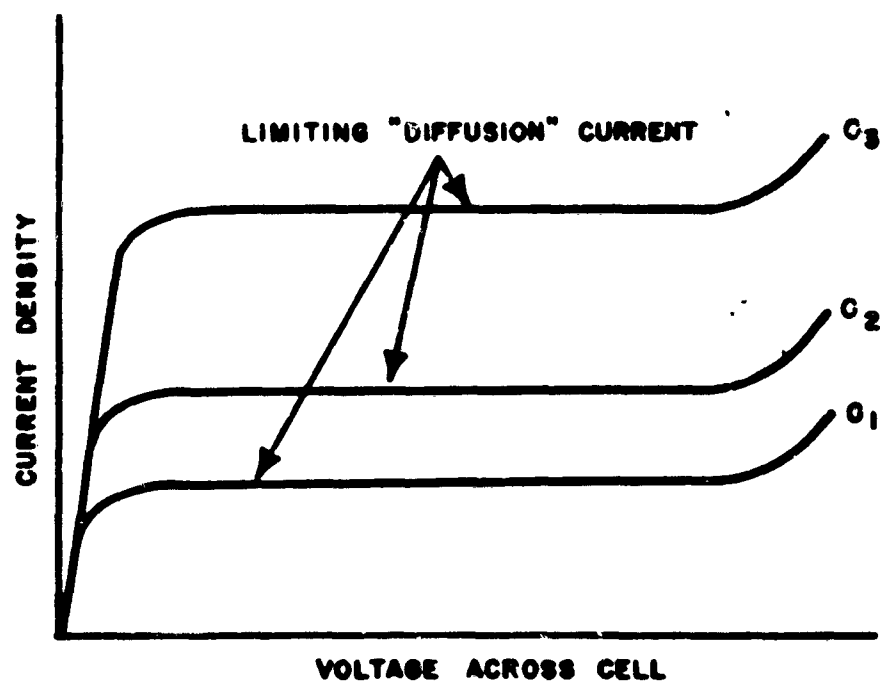


FIG. 2

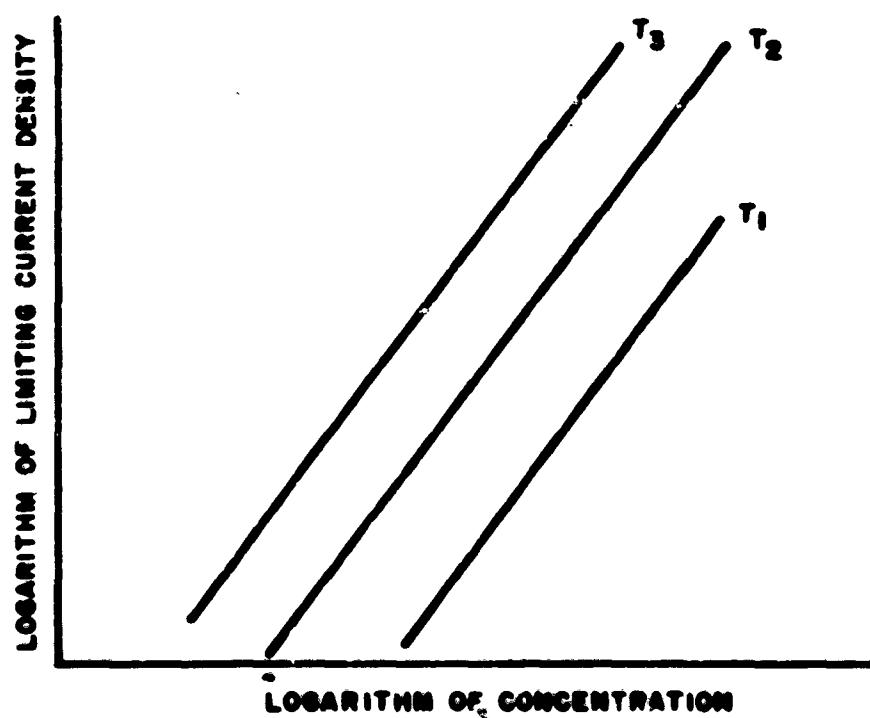


FIG. 3

That amount of triiodide ions reduced electrochemically at the cathode is regenerated at the anode, maintaining the triiodide ion balance. Although within the cell there is no net change in triiodide ion amount, the local concentrations of triiodide ions can vary considerably, i.e., the triiodide ions can be moved about within the cell virtually at will.

Let us look at these relations more critically. Figure 3 shows a relation of the form

$$J = kC^{\gamma} \text{------(4)}$$

where,  $J$  = current density (cathodic)  
 $k$  = constant for given conditions  
 $c$  = concentration of triiodide ions  
 $\gamma$  = constant ( $\approx 1.25$  for a cell such as in figure 1)

We have, then, a relation between current density and concentration. Unfortunately, this relation holds only for vertical, plate-like electrodes in unstirred solutions in which natural convection can occur. Other geometrical arrangements subjected to natural convection and other methods of mass transfer will give a different relationship. The convecto-diffusive mass transfer problem has been solved for this case (1). The result is

$$J = 0.525F \left( \frac{g \alpha D^3}{\nu l} \right)^{0.25} c^{1.25} \text{------(5)}$$

(1) Agar, J. N. Disc of Faraday Society, 1, 26, 1947

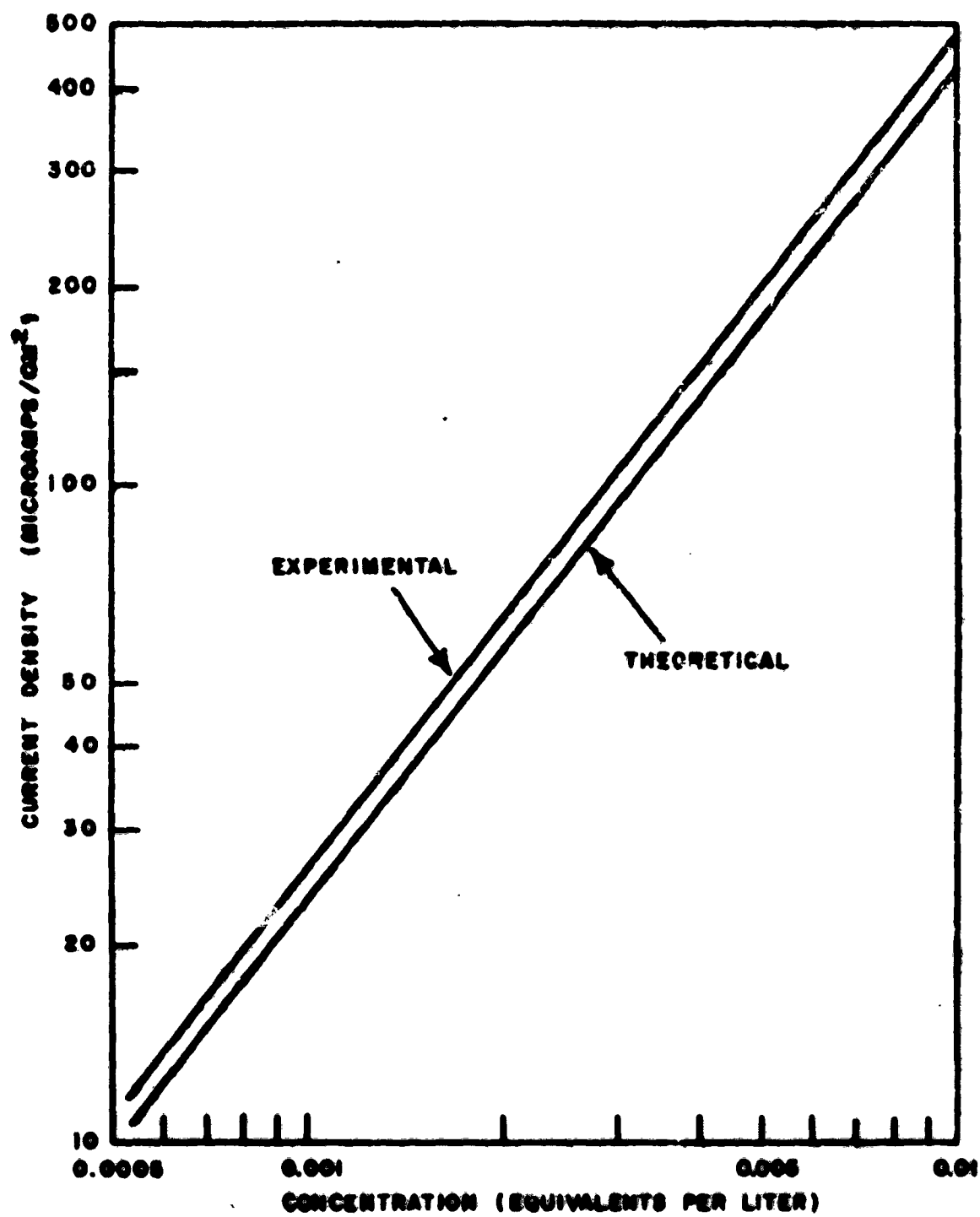
where  $J$  = cathodic current density  
 $F$  = Faraday's constant  
 $g$  = acceleration of gravity  
 $\alpha$  = density coefficient (see below)  
 $D$  = diffusion coefficient  
 $\nu$  = kinematic viscosity  
 $l$  = electrode diameter  
 $C$  = triiodide ion concentration in bulk of solution

and,

$$\alpha = \frac{\rho - \rho_0}{\rho_0}$$

where  $\rho$  = density at bulk concentration of triiodide ion  
 $\rho_0$  = density of solution at zero concentration of triiodide ion  
 $C$  = triiodide ion concentration in bulk solution.

Figure 4 compares the semi-theoretical and actual curves. Checks are obtained within the measurement errors, especially those of determining the value of  $\alpha$ .



**FIG. 4 COMPARISON OF EXPERIMENTAL LIMITING CURRENT WITH EQUATION 5**

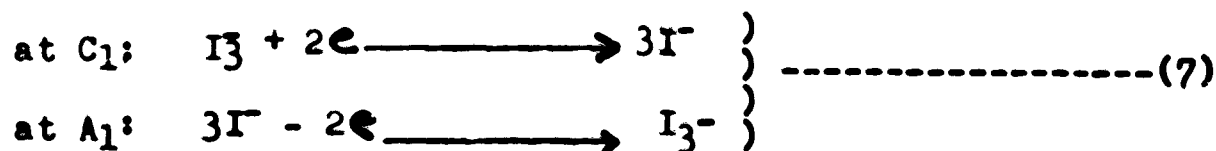
If the distance between the electrodes is reduced appreciably while maintaining the electrode area, eventually convective effects are considerably reduced, and the mass transfer becomes diffusion controlled. The linear diffusive equation is easily solved, giving the predicted cathodic current density as

$$J = \frac{2FDC}{L} \left\{ 1 + 2 \sum_{n=1}^{\infty} e^{-\left(\frac{2n\pi}{L}\right)^2 Dt} \right\} \text{-----}(6)$$

where L = electrode spacing  
 t = time  
 n = summation index  
 C = concentration of triiodide

Note the steady state term. This arises from the current "feed-back" from cathode to anode. It is only of importance for closely spaced electrodes. Thus, in a large cell, such as in figure 1, diffusion alone would not predict a steady state current, whereas in a "microcell", it does. Note the linear relation between concentration and current density. (The microcell is used in all NOL work where integration is the prime requirement.)

Consider now the hypothetical arrangement shown in figure 5 (a) with the switch (SW) initially in position B for some time. Consider the small chamber at the right to be within the dimensions of a diffusive system as previously described, and that initially the triiodide ions within it are essentially zero, i. e., the solution within this small chamber is essentially KI in water. Also consider that the area of C<sub>1</sub> is so large and the bulk concentration of triiodide ion so great that the current flowing through it will be limited by R when the switch is finally thrown to position A, and not by the limiting currents of figure 2. In other words, the major voltage drop will be across R when the switch SW is flipped to position A. When SW is finally closed in position A, triiodide ions are reduced at C<sub>1</sub> and an equal number are generated at A<sub>1</sub>:



After an initial delay, the current in M<sub>2</sub> starts to rise. With the current in M<sub>1</sub> constant, the current in M<sub>2</sub> obeys the following time relation:

$$\frac{I_{M_2}}{I_{M_1}} = \frac{2Dt}{L^2} - \frac{1}{6} + \frac{8D}{L^2} \sum_{n=1}^{\infty} e^{-\left(\frac{2n\pi}{L}\right)^2 Dt} \left\{ t + \frac{L^2}{(2n\pi)^2} \cdot \frac{1}{D} \right\} \text{--}(8)$$

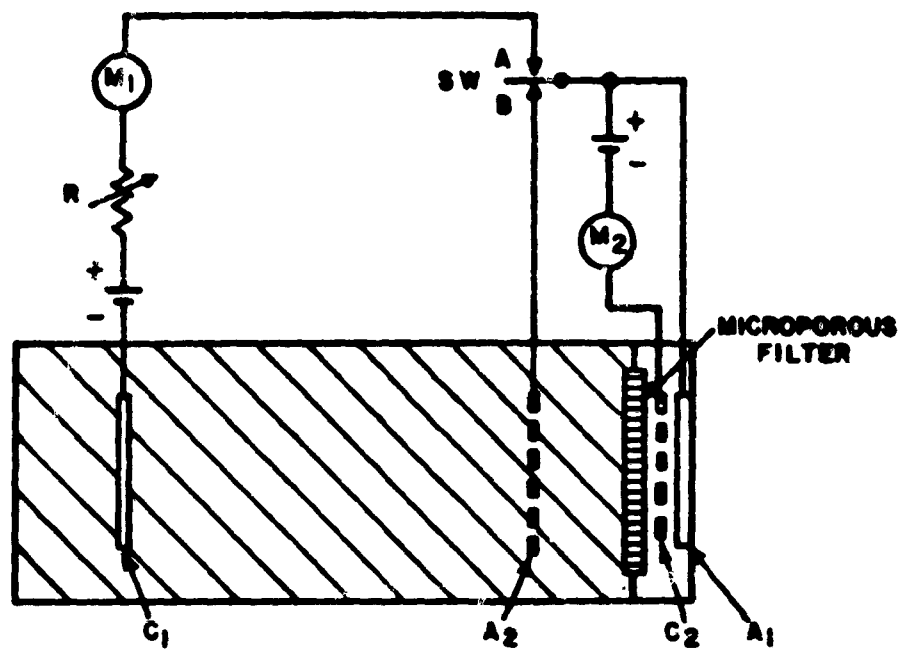


FIG. 5a

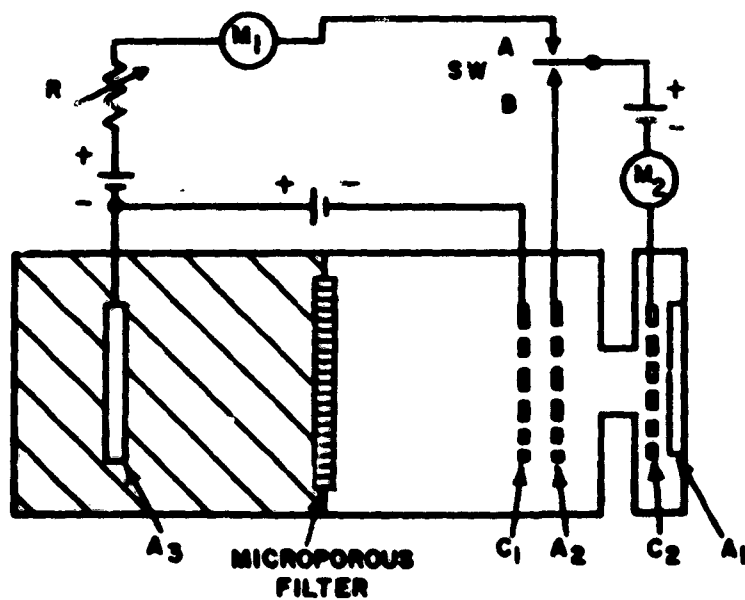


FIG. 5b

# DIAGRAMMATIC ELECTROCHEMICAL INTEGRATOR CIRCUITS



where,

$I_{M_2}$  is the current observed in  $M_2$

$I_{M_1}$  is the current observed in  $M_1$

For  $D = 1.5(10)^{-5} \text{ cm}^2 \text{ sec}^{-1}$  (a value about 30% - 40% high for iodide-triiodide solutions in methanol) and  $L = 0.0025$  and  $0.003$  inches, this expression is applicable for times greater than about 0.1 and 0.2 seconds. This relation is plotted versus time in figure 6 for  $D = 1.5(10)^{-5} \text{ cm}^2 \text{ sec}$ . Note the linear integration region after 0.3 - 0.4 seconds.

If we define an "integrator coefficient" as

$$\frac{\frac{d}{dt} (I_{M_2})}{I_{M_1}} = \text{"integrator coefficient"}$$

its value becomes

$$\text{Int. coeff} = \frac{2D}{L^2} + \frac{8D}{L^2} \sum_1 \left[ -\left(\frac{2n\pi}{L}\right)^2 D e^{-\left(\frac{2n\pi}{L}\right)^2 D t} \left\{ t + \frac{L^2}{4n^2 D} + e^{-\left(\frac{2n\pi}{L}\right)^2 D t} \right\} \right]$$

----- (9)

A plot of this relation for the same values of  $D$  and  $L$  as previously given in figure 6 gives the results shown in figure 7. Experimentally, however, this coefficient can be determined by integrating for a time over the linear portion of the integration curve, allowing for the initial delay. The coefficient is the slope of the reduced curves of figure 6 in this linear region. The curve will continue to rise after shutting off the input for a time about equal to the initial delay time.

A typical experimental integrator response curve for the iodine-iodide system in methanol solvent is shown in figure 8.

The sketch of figure 5a is schematic only. It should, however, convey the essential features of electrochemical integration without the complexities of an application problem. In the actual operation, however, the concentrated triiodide solution is further removed from the integration volume, and the microporous filter between the bulk solution is omitted,

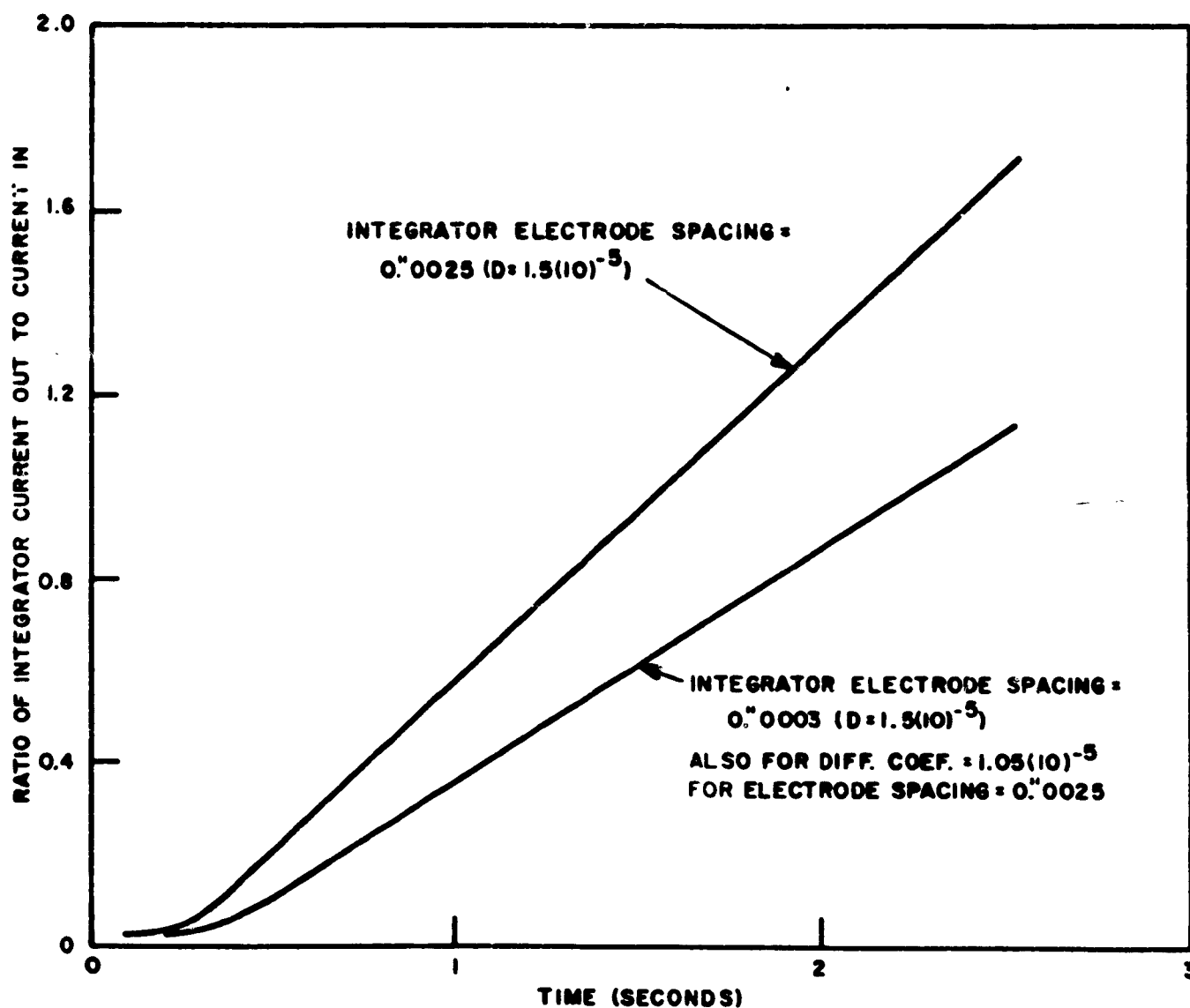


FIG. 6 INTEGRATOR RESPONSE AS A FUNCTION OF TIME FOR DIFFUSION COEFFICIENT EQUAL TO  $1.5(10)^{-5} \text{ CM}^2 \text{ SEC}^{-1}$  AND EQUAL TO  $1.05(10)^{-5} \text{ CM}^2 \text{ SEC}^{-1}$

$$\frac{I_{OUT}}{I_{IN}} = \frac{2Dt}{L^2} - \frac{1}{6} + \frac{8D}{L^2} \sum_{n=1}^{\infty} e^{-\left(\frac{2n\pi}{L}\right)^2 Dt} \left\{ t + \left(\frac{L}{2n\pi}\right)^2 \cdot \frac{1}{D} \right\}$$

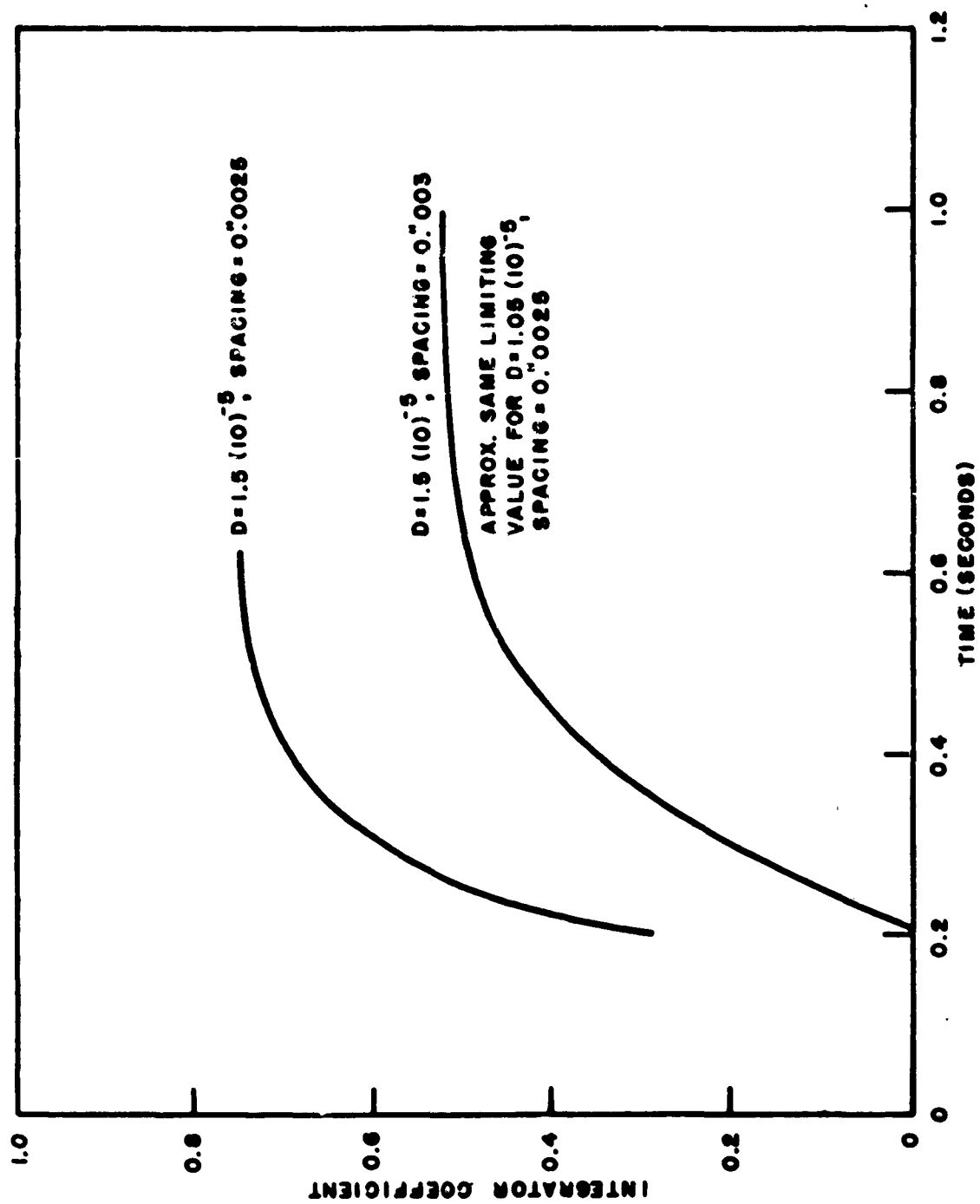


FIG. 7 INTEGRATOR COEFFICIENT FOR VARIOUS SPACINGS AND DIFFUSION COEFFICIENTS

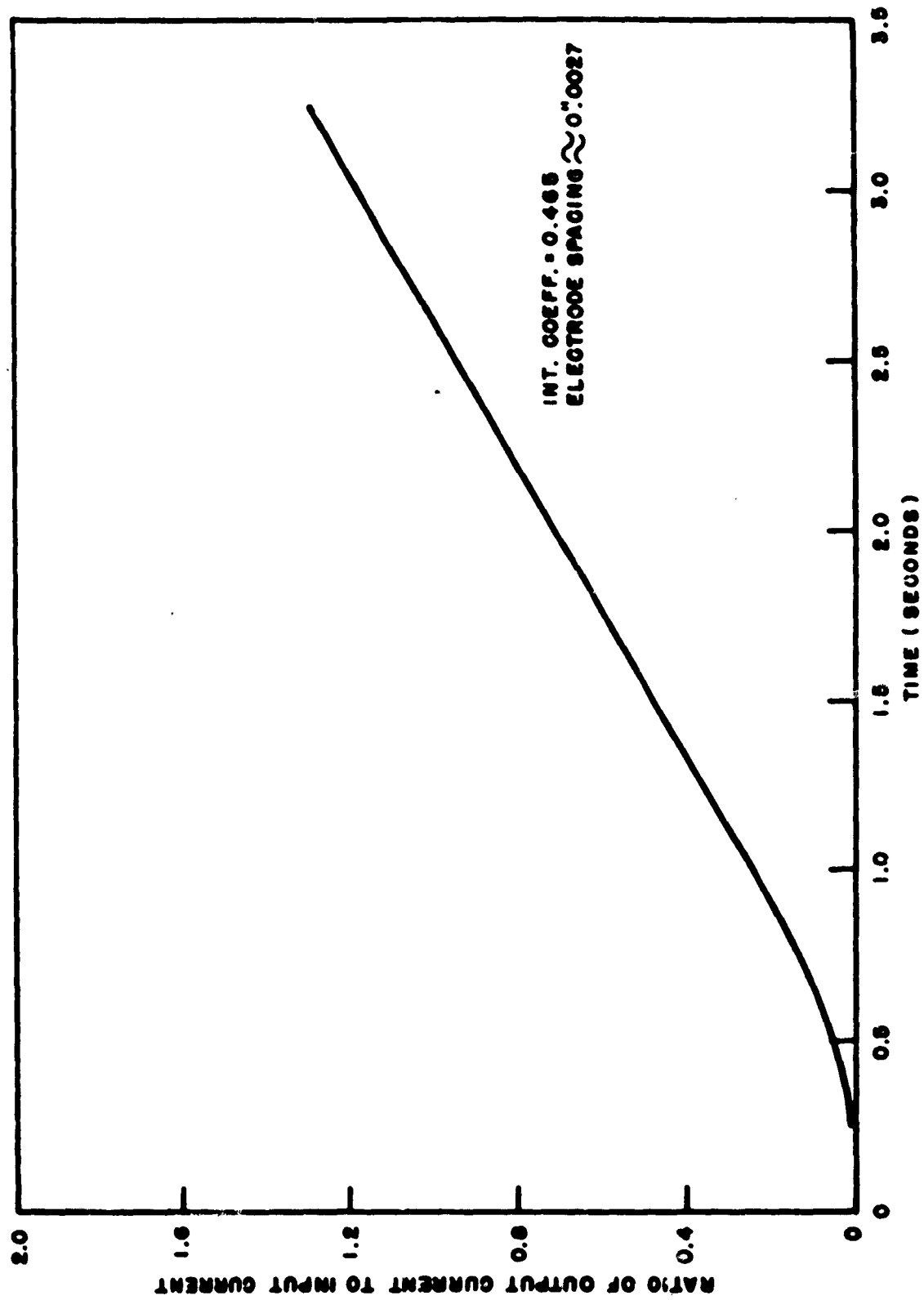


FIG. 8 EXPERIMENTAL INTEGRATION CURVE

being replaced by a geometric restriction. A typical unit setup for determining integrator response and integrator coefficient is shown diagrammatically in figure 5b. Of course, the input current to an integrator of this type may arise from a number of sources. One of which may be an electrochemical (acoustic, etc.) transducer which may be part of the same unit.

Many redox systems are suited for this application. Their selection depends upon the desired end use. Some of these systems are:

Cerate - Cerous systems  
Thallic - Thallous systems  
Bromine - Bromide systems  
Ferricyanide - Ferrocyanide systems

An important design variable is the diffusion coefficient, D. The value of D may be estimated from the well-known Stokes-Einstein equation for spherical particles:

$$D = \frac{kT}{6\pi r\eta} \text{ -----(10)}$$

where

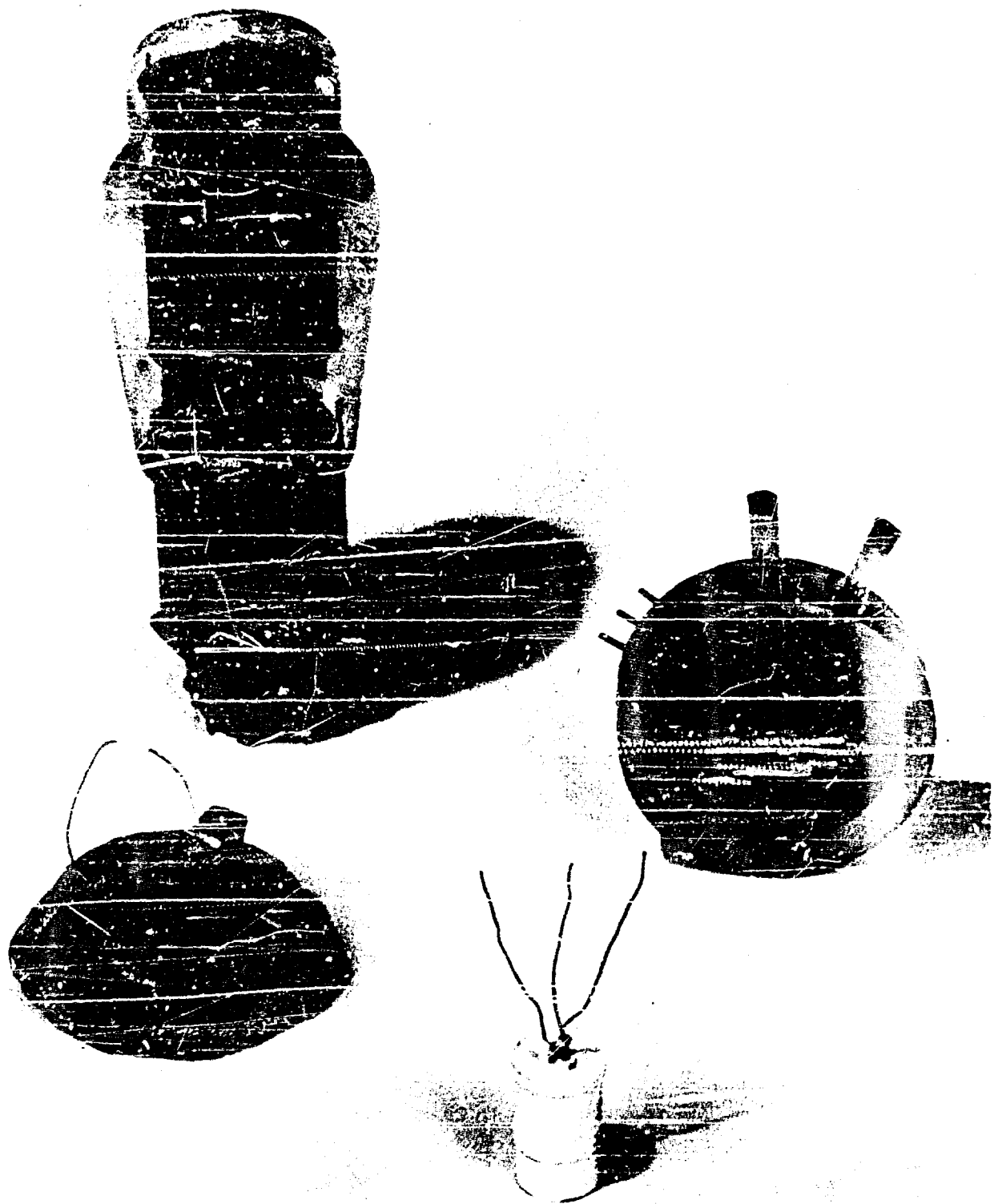
D = Diffusion coefficient  
k = Boltzman's constant  
T = Absolute temperature  
r = Ionic radius (including solvation)  
 $\eta$  = Viscosity coefficient of the solution.

Roseveare, Powell and Eyring (2) have extended this analytical relation between diffusion and viscosity.

The analysis of electrochemical integrators just presented does not allow for "integrator leakage" due to diffusion from the integrator. The amount of leakage in one application using iodine-iodide solutions in methanol, and a relatively accessible integrator is somewhat less than 0.3 percent per second. This of course is an easily controlled design function of such integrators. The analytical considerations can be extended to include these variables with moderate difficulty.

The voltage limitations of reversible electrochemical solutions must be observed. Figure 2 shows a current rise at higher voltages. This destroys the reversibility of the solutions and must be avoided.

(2) Roseveare, W.E., Powell, R. E., Eyring, H., Ind.Eng Chem, 33, 430 (1941)



Technical Information Division  
Naval Ordnance Laboratory  
Silver Spring, Maryland  
18 July 1957

REFERENCE NOTES ON THE SOLION,  
A VERY LOW POWER ELECTROCHEMICAL CONTROL UNIT

There appears to be no completely organized body of formal literature in the English language giving technical details on the solion. Best source of what basic information is available at this date is contained in a brochure published recently by this agency entitled simply SOLION.

The solion is an electrochemical device based on the principle of concentration polarization. Essentially it is composed of a plastic cylinder with flexible end walls and containing a solution of potassium iodide and iodine. In this solution several platinum or other noble metal electrodes are immersed. Polarization is by means of a low voltage (0.9 v) battery. Stimulation of the diaphragms at each end causes an hydraulic flow which results in current flow. This process is reversible. The unit is sensitive to stimulation by heat, light, sound, pressure and motion. Size is not critical as to external dimensions, although distances between electrodes may be. Solions to this date have been produced only by Emhart Manufacturing Company, Hartford, Conn. There now exists a small production contract with the Minneapolis-Honeywell Regulator Company, Minneapolis, Minn. Contract negotiations also have been under way with National Carbon Company, 20 East 42nd Street, N.Y.C.

Commercial applications of the solion are one of the interests of the Texas Research Associates, Box 7095 University Station, Austin, Texas. This device was initially developed by the Naval Ordnance Laboratory under the supervision of Nelson N. Estes. Associated with NOL scientists in this, under a Bureau of Ordnance research and development contract, is the Defense Research Laboratory, University of Texas. DRL people particularly active in this are H. D. Krick, R. N. Lane and R. M. Hurd. After Mr. Estes leaves NOL August 2, 1957 to join Texas Research Associates work on solions largely will be under supervision of Donald W. Kuester.

Information contained in the NOL publication SOLION is divided into four parts as follows:

1. Introduction & history, including patent information, by H. B. Reed, NOL.
2. Principles of Electrochemistry Basic to Electrolytic Systems, by R. M. Hurd of DRL.
3. Principles of Very Low Power Electrochemical Devices, by R. N. Lane, TRA.

4. Principles of Electrochemical Integrators, by H. B. Reed.

Although further information on the solution will be published by NOL and others as research continues, the data contained in the above is as complete a coverage of the subject as can be had at present in an unclassified document. Other technical information now available for persons having the "need to know" required by security regulations is contained in certain progress reports issued in recent years as research work progressed.

The classified reports referred to above can be made available through the library of this agency. Persons desiring this service should make a request direct to the Library, Naval Ordnance Laboratory, Silver Spring, Maryland, through the security channel they normally use for such purposes. These reports are entitled as follows:

1. Vols. I, II and III of Summary Report of Contract NOrd-10639, by Staff of Acoustics Division, Defense Research Laboratory, 29 September 1955.
2. Monthly progress report for July, 1955, Contract NOrd-10639, by Staff of Acoustics Division, DRL, 10 August 1955.
3. Defense Research Laboratory acoustical report No. 100 by K. W. Hannah, 6 January 1956.

Patents have been issued to four individuals on various aspects of the solution and some 27 are pending before the U. S. Patent Office, a number of them under a secrecy order.

Patents issued are as follows:

1. No. 2,526,670 - Kissinger et al, electrolytic switch, government royalty free license.
2. No. 2,585,025 - Root et al, electrolytic device, government has license in Claim One and nothing in Claim Two.
3. No. 2,705,919 - Scafo, filter, govt royalty free license.
4. No. 2,760,993 - Coff. electrolytically controlled extender delay device for line, complete government title.

Although no information can be given out concerning patent applications pending it is stated here that there is nothing involved that would restrict commercial application under the usual license agreement. The same applies to patents granted.



The name "solion" (pronounced soh-lee-on), as a name for these low power electrochemical sensing and control devices, is simply short for "ions in solution". The term appears in technical literature printed after 1 June 1957. Prior to that month it had no name, but was referred to as an "electrochemical device". It is the product of the new technology now named "chemtronics", an applied branch of electronic science dealing with the movement of ions in solution rather than electrons in space, as in a vacuum tube, or in a solid as in transistors. Both names were arbitrarily assigned to the item and the technology, respectively, in an NOL information memorandum dated 18 June 1957. The name "solion" has been widely published in both technical and consumer news media and in very recent technical brochures. It appears accepted by common consent. It can be freely used without fee and is not part of any patent or trademark.

ECI 16 July 1957